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SULPHUR

THE MAGAZINE OF WORLD SULPHUR

contents

	page
Expansion in Argentina's Sulphur and Sulphuric Acid Industries	1
Single Stage Leach Process for Zinc Concentrates: Sherritt Gordon's new method	8
Occurrence of Sulphur Deficiency States in Brazilian Coffee Plantations	12
U.K. Brimstone Imports in First Half of 1961 Highest on Record	14
Alkali Inspector's Report: Emission of acid mist in waste gases still a problem	17
Overcoming SO_2 Pollution Problems in the U.S.A.: Stauffer research on control techniques	19
Titanium Dioxide Extraction by Continuous Process: Soloducha-Continental Titanium method offers flexibility and economy	21
Sulphur Ore Treatment at the Rozdolski Plant: U.S.S.R. brimstone production now 1.4 million tonnes	22
Prices and Trends: Growth of world sulphur consumption temporarily halted	24
Fluor Solvent H_2S/CO_2 Process for Wintershall AG.	31
Berk Commissions New Sulphuric Acid Plant	34
Dimethyl Disulphide for Solvent Extraction of Sulphur	35

CURRENT EVENTS

Canada	BA Sulphur Recovery Plant	39
	Sulphur Production at Carstairs	39
United States	Stauffer's New Route to SO_2	40
	Uranium Processing by Petromics	40
	Virginia-Carolina Interest in Texas International Sulphur	41
Norway	Sulphuric Acid Production to Increase	41
Italy	Sulphur Refining Plant at Licata	41
France	Cie St. Gobain's New Acid Plant	42
Yugoslavia	Bor Phosphate and H_2SO_4 Plants	42
U.S.S.R.	Automatic Acidity Control in Ammonium Sulphate Manufacture	43
Czechoslovakia	Sodium Pyrosulphite from SO_2 in Waste Gases	43
Japan	Titanium Dioxide Production Difficulties	44
	Chugoko Sangyo's New Process for CS_2	44

COMPANY REPORTS

Laporte Industries Now Reaping Benefit From Increased Output of Titanium Dioxide	45
Ketjen Reports Sulphuric Acid Plants Worked at Full Capacity in 1960	46
Courtaulds Group Profit Affected by Increased Competition and Slackening Demand	47
Statistical Appendix	48
Index to Advertisers	xix

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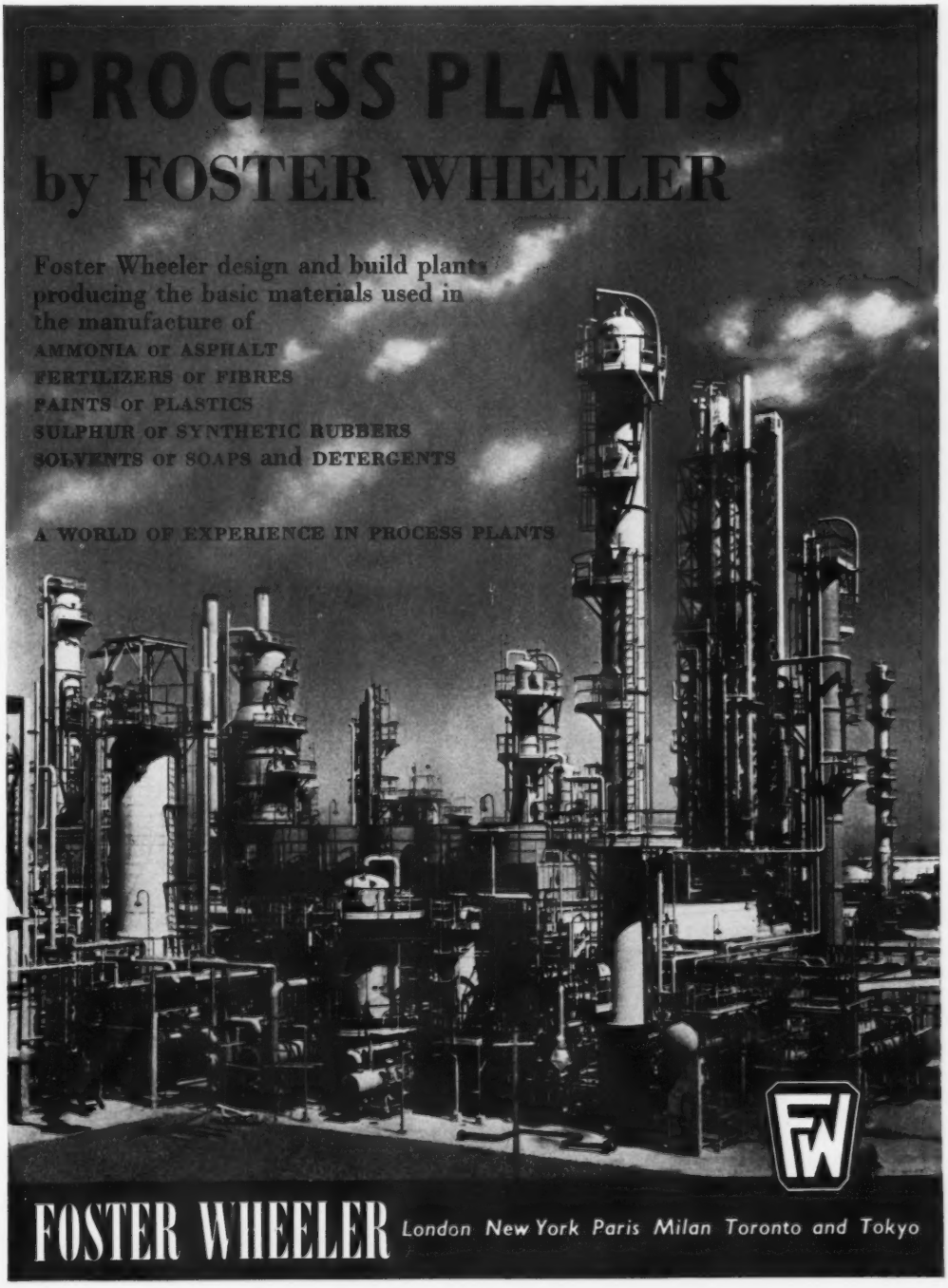
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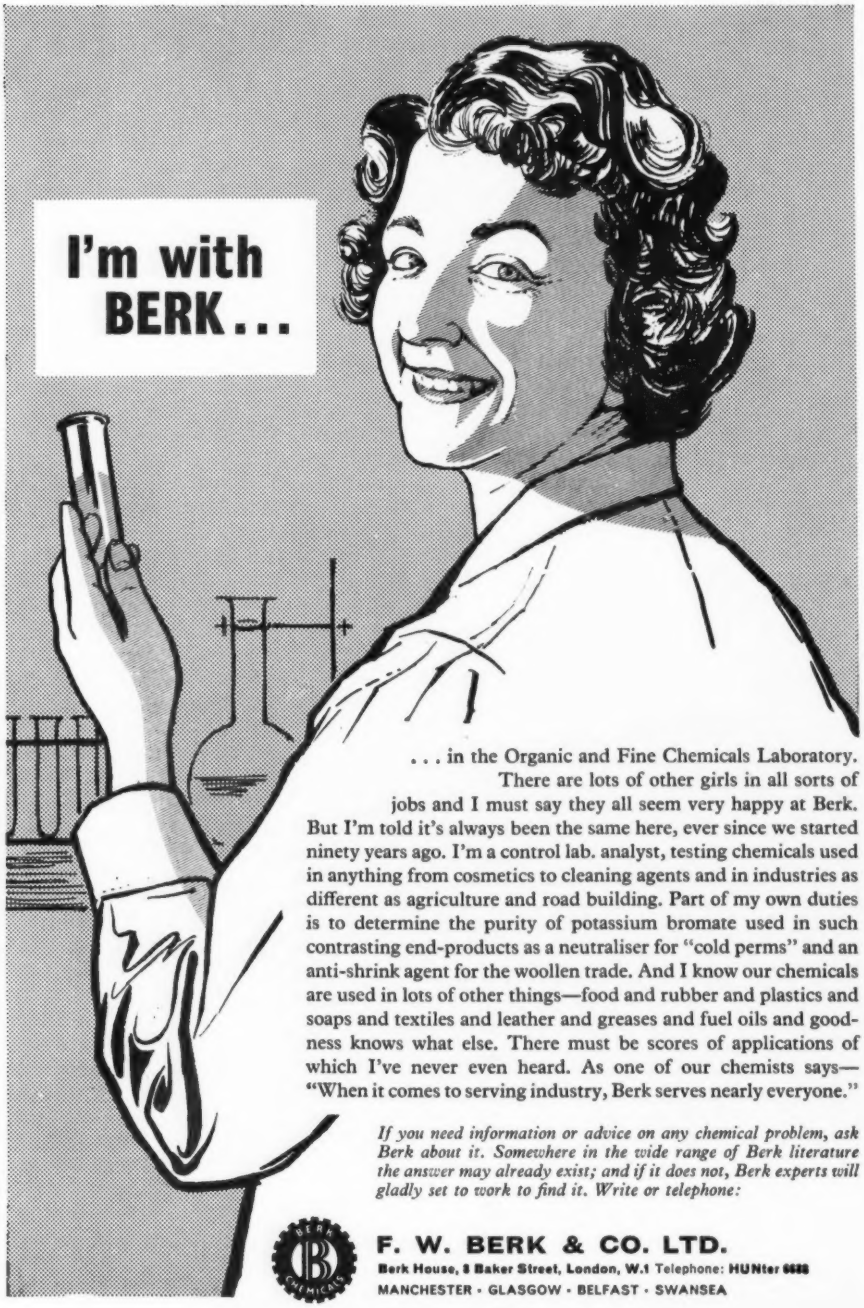

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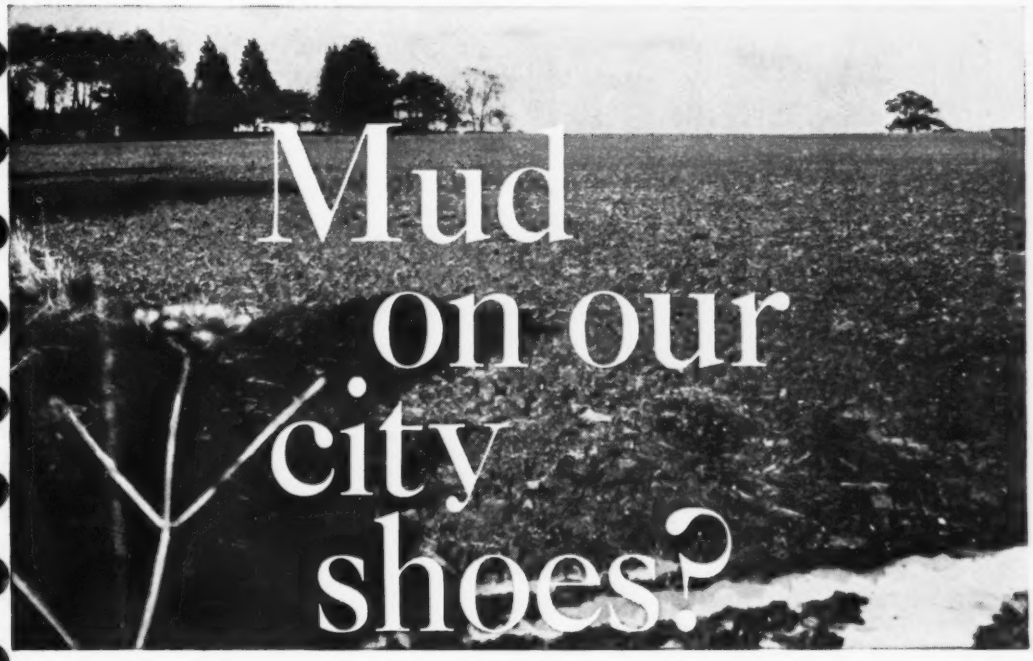

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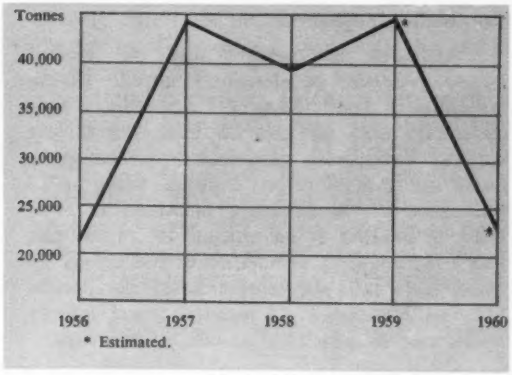
Expansion in Argentina's Sulphur and Sulphuric Acid Industries



Argentina's sulphur imports 1956-1959

THE POLITICAL and economic renaissance of the Argentine which may be said to have started with the fall of the Peron Government in 1955, but which has been delayed during several years of political changes and by the economic difficulties resulting from the need to stabilise the currency and re-establish a favourable investment climate, now appears to be evident.

The Argentine is rich in natural resources and having now a sufficiently large population without being too densley populated — 20 million inhabitants or seven persons per square kilometre and population increasing at 1.9% annually — the prospects of rapid economic growth are good. Of the country's gross national product in 1957 agriculture accounted for 19% and manufacturing 22%. The present Government's efforts centre on expanding the GNP rapidly after a long period of near stagnation culminating in 1958/9 in heavy inflation but which has since been arrested. Agriculture supplies about 25% of the population and there is a well-established, although still small-scale, industrial activity. The chemical industry in particular is playing an increasing part and the sulphur and sulphuric acid sectors are at the start of a new expansion phase. The two strongest stimuli to the country's economic growth and to the sulphur industry is the rapid development of the Argentine's oil resources and the establishment of a steel industry.

Extensive Sulphur Deposits

Argentina has extensive deposits of native sulphur along the upper slopes of the Eastern Andes. These have been exploited for a number of years, partly for fused sulphur production and partly for direct use of the ore (Caliche) in sulphuric acid manufacture. In addition sulphur dioxide in exit gases of zinc smelters, based on native zinc blende, is used for sulphuric acid production and more recently hydrogen sulphide extracted at a new coke oven plant helps to boost indigenous sulphur supplies.

Notwithstanding these resources more than one half of the Argentine's sulphur requirements are imported in the form of brimstone from the Frasch sulphur mines in the U.S.A. and more recently Mexico.

Sulphur Mining

At present four sulphur mines are being exploited and the mine output is in the form of caliche (35% to 50%) sulphur. In 1958 this amounted to 80,127 tonnes and in 1959 about 75,000 of which about 40,000 tonnes and 45,000 tonnes respectively is estimated to have been refined and the balance delivery *tel quel*. Following a full year's production at the new plant at Sominar total production of brimstone in 1960 is estimated at 28,000 tonnes.

Sulphur Production

1943	9,001	1952	18,551
1944	11,138	1953	10,001
1945	11,534	1954	20,269
1946	10,093	1955	18,162
1947	10,907	1956	18,500
1948	8,384	1957	17,300
1949	10,071	1958	18,000
1950	7,785	1959	*20,000
1951	7,681	1960	*28,000

* Estimated.

Soc. Minera Argentina

Although at present only the second largest producer of elemental sulphur in the Argentine, Soc. Minera Argentina S.A. (Sominar) may be said to have the largest sulphur production potential. The company owns the Volcan Overo Sulphur Mine at El Sosneado, in the province of Mendoza. The mine is situated at an altitude of 14,500 feet and this, coupled with climatic conditions — heavy snow falls and storms during the months May to November — restrict actual mining operations to only four months of the year.

Volcan Overo Sulphur Mine

The deposit is of volcanic origin and the average grade of the ore is about 35% sulphur. Mining is by opencast methods. The ore is loaded from the working faces by caterpillar excavators to trucks for transport to the bins of the loading station of an aerial tramway some 2 to 6 kilometres distant.

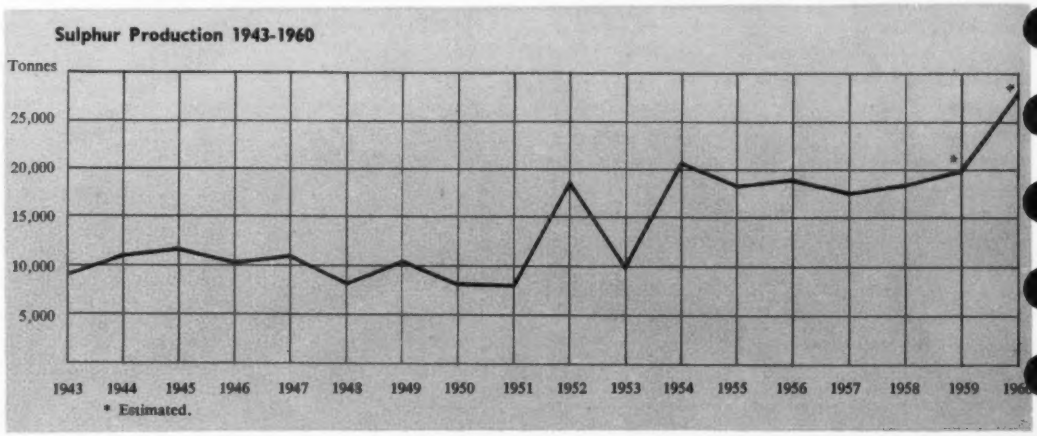
Ore is transported by an aerial tramway from the mine to the treatment plant which is located on the east bank of the Atuel River at an altitude of 2,400 metres above sea level. The aerial tramway—a bi-cable type with an hourly capacity of 30 tonnes—is 11.6 kilometres in length with a difference in elevation of 2,100 metres between the loading and unloading stations.

At the unloading station, the ore is delivered to a stock pile from which plant feed is obtained through feeders and a conveyor belt installed in a tunnel under the stock pile.

Sulphur Refining Plant. The plant, designed by Chemical Construction Company of New York, embodies this company's sulphur refining process which entails autoclave treatment of crushed ore, flotation of the undersize material discharged from the autoclave and pressure filtering of the resultant 95% sulphur product to yield 99.5% S material.

The sulphur refining plant, too, normally operates only seven months during the year due to the adverse climatic conditions. Ore is reduced by two-stage crushing and wet grinding to pass a 28 mesh screen. After adjustment to a 30% solid content, the slurry is pumped to a continuous autoclave consisting of three compartments, each fitted with a motor-driven agitator, in which the slurry is heated by steam injection in the bottom of each compartment to 130°C at a pressure of 55 p.s.i.g.

As a result of the heat and agitation, the sulphur particles melt and separate from the gangue forming globules of liquid sulphur. Some of these globules collide during agitation and agglomerate, making them larger than the gangue particles. To maintain the water as a liquid, the autoclave is pressurized with air to a theoretical pressure of at least 40 p.s.i.g.; in practice, about 50 to 60 p.s.i.g. is used. Hot slurry from the autoclave flows into a quench pot fitted with a motor driven agitator where it is quench-cooled by the injection of cold water. The sudden cooling solidifies the separted molten sulphur particles. Cooled slurry is throttled to atmospheric pressure through a motor-operated slurry throttle valve controlled by the slurry level in the quench



pot. Instrumentation is used for the control of the autoclave, quench pot and throttle valve.

Cooled pulp is passed over a 28 mesh screen where the oversize material which is normally about 95% sulphur is sent directly to the flotation circuit from which a concentrate of about 95% sulphur is obtained. The concentrate after dewatering on a horizontal filter is discharged to the sulphur melting pit. All equipment which is in direct contact with the slurry is constructed of stainless steel.

Liquid sulphur from the melting pit is pumped by means of an air-pressurised blow case to a pressure filter where the remaining gangue is retained on the filter leaves and a finished grade of sulphur is discharged in liquid form which is allowed to solidify in the open air. The cake from the pressure filter containing about 50% S is recycled through the plant.

Important factors in the operation of the plant are pH of the slurry, temperature and agitation in the autoclave and quench pot, retention time and pulp densities. The pH is controlled by the addition of lime to the wet grinding circuit. The flotation reagents used are pine oil and diesel oil. Settlement in the middlings thickener and the tailings thickener is aided by the addition of animal glue. Clear hot water from the thickeners is recycled for use in the plant.

The plant was designed to produce 50 tonnes of 99.5% sulphur per 24 hours when treating 186 tonnes of ore containing 30% sulphur. Overall recovery is 90%.

During the period November 1959 to May 1960 the plant produced approximately 10,000 tonnes brimstone and it is estimated that during the current season a similar tonnage will be produced. The bulk of the mine's output of caliche was supplied *tel quel* to a number of sulphuric acid plants but in future this practice is unlikely to continue as transporation costs and the large distances involved makes this form of sulphur uneconomic and there is no inducement to augment mine production in excess of the needs of the ore refining plants.

La Casualidad. This mine situated in the province of Salta is operated by the Direccion General de Fabricaciones Militares which, in addition to a number of mining enterprises, also administers several industrial plants including chemicals, supplying in the first place the needs of the armed forces but also public requirements.

Mining operations which are carried on at a height of over 14,000 feet, are limited to a few months of the year. At present virtually the entire output of the mine estimated at 40,000 to 45,000 tonnes (caliche) with a sulphur content of over 50% is converted into fused sulphur in autoclaves and the production in 1959/60 season amounted to 18,000 tonnes pure sulphur.

Fabricaciones Militares has recently commissioned a Japanese company to modernise and expand the sulphur refining installations at La Casualidad. In 1961 or at the latest in 1962, it is expected that capacity will have been raised to 30,000 tonnes a year.

Other Mines

Cerro Bayo. This small mine situated near Chos Malal in the province of Neuquen produces currently at an annual rate of 400 to 500 tonnes sulphur based on autoclave refining of very low grade ores. Also based on autoclaves is the small scale production at the *Betty Mine* in the province of Salta. Some years ago ore from this mine was refined by a carbon disulphide solvent process which was discontinued as being uneconomic.

Recovered Sulphur

The Oil Refinery installations of Yacimientos Petroliferos de Fomento (YPF) are to include an H_2S extraction and sulphur recovery unit. It is to be built by Parsons Powergas Company of Stockton-on-Tees.

The plant will handle an acid feed gas to produce 42 long tons per day of sulphur with a minimum purity of 99.5% at a recovery efficiency of not less than 95%. The plant is due to be completed in 1962.

By-product Sulphuric Acid

Zinc smelter operations by Fabricaciones Militares and Sulfacid S.A. are combined with sulphuric acid manufacture based on SO_2 contained in zinc smelter exit gases. Installed capacity at the two plants is approximately 47,000 tonnes 100% H_2SO_4 of which it is estimated that only 80% is employed. Sulfacid S.A. is reported to be contemplating the installation of a second by-product sulphuric acid unit which is to be combined with a new zinc

smelter in which St. Joseph Lead Company may be taking a share.

At San Nicolas Steelworks there is a wet contact sulphuric acid plant with a daily capacity of 13.5 tonnes (78% H_2SO_4) built by Chemiebau Dr. Zieren of Cologne to utilise H_2S extracted from coke ovens. Early this year this state-owned steel plant was expanded. The new coke oven battery built by Pintsch-Bamag G.m.b.H. of Berlin includes gas treatment facilities for by-products, and hydrogen sulphide is extracted in an Alkazid installation. A wet contact sulphuric acid plant with a daily capacity of 10 tonnes is due to stream this year.

Up to 1959 the City Gas Company of Buenos Aires operated a chamber plant with a capacity of 40,000 tonnes. It was based on spent oxide resulting from the town gas manufacture. As the city's gas supply is now based on natural gas this plant was dismantled.

Imports

Up to 1958 the entire import requirements of the Argentine were met by Frasch sulphur supplies from the U.S. In 1959 Mexican sulphur first entered the Argentine with deliveries of 4,048 tonnes by Pan American Sulphur Company, and 9,767 tonnes by Gulf Sulphur Corporation and U.S. Frasch sulphur accounted for 69% of total imports. By 1961 no Mexican sulphur appears to have entered this market and lower demand coupled with greater domestic output reduced total import needs by almost one half. This year imports are expected to rise to about 35,000 tonnes.

IMPORTS

Tonnes

1956	1957	1958	1959	1960
21,632	43,995	39,239	*44,300	*23,000

* Estimated

Sulphur Prices

Reflecting the general trend of liberalisation of the Argentine economy the domestic sulphur market is free. Imported sulphur in recent months had landed at $31 per tonne. The Argentine Government levies on sulphur imports a surcharge of 100%; thus at the current exchange rate which is also free and has in recent month been stable at about Pesos 83 to the U.S. $, the local price of imported sulphur is Pesos 5,100 per tonnes ex loading station. Domestic sulphur has to compete with imported material at this price level and as the bulk of sulphur consumption is in the Buenos Aires area, domestic sulphur producers suffer from the full impact of high transportation costs over a distance of over 650 miles and which in 1959 had been raised by 100%. It is reported that domestic producers have asked the Government to increase the surcharge on imported sulphur but for the time being no significant change is expected and in keeping with its policies it is virtually certain that no quota restrictions on imports, nor legislation to favour indigenous productions will be promulgated by the Government.

Sulphur Consumption

Current level of sulphur consumption in all forms in the Argentine is estimated at 75,000 tonnes annually. Of this 60,000 tonnes is in the form of brimstone and the balance mainly sulphur dioxide contained in zinc smelter gases augmented by hydrogen sulphide extracted at coke ovens. Caliche (50% S ore) of which in 1959 35,000 tonnes was burnt in sulphuric acid manufacture, is no longer being used in significant quantities but one of the zinc smelters intends to augment the SO_2 content of roaster gases by burning some of this material. Sulphur demand is determined almost exclusively by industrial activities other than fertilizer.

Fertilizers. Hitherto due to the exceptional fertility of the Argentine pampas very little fertilizer has been used on the main agricultural crops and the limited domestic production and the imported fertilizer are used in horticulture, fruit, vines and to certain extent sugar cane.

Total fertilizer sales are estimated at about 100,000 tonnes of which one-half are compounds. Fertilizer production has been confined to the manufacture of single superphosphate — almost 9,000 tonnes in 1958/59 — and about 40,000 tonnes organic fertilizer. In 1958 the Fabricaciones Militaires brought on stream a 23,000 tonnes (100% H_2SO_4) brimstone acid plant the output of which is destined for fertilizer manufacture, ammonium sulphate and some superphosphates. By-product ammonium sulphate is also being produced at the San Nicolas steelworks in plant with a daily capacity of 21 tonnes.

Viscose. The largest single sulphur consuming industries are the manufacturers of rayon and cellulose film who in 1959 are

estimated to have consumed 21,000 tonnes sulphur in the form of sulphuric acid and carbon disulphide.

Other Consumers. Other prominent sulphur consumers are the oil refineries, manufacturers of water treatment compounds and chemical, manufacturers all of whom use it in the form of sulphuric acid.

Sulphuric Acid

Total employed sulphuric acid capacity in the Argentine is reported at 164,000 tonnes 100% H_2SO_4, represented by eleven plants including two wet contact acid plants mentioned above. The main producers are:—

Fabricaciones Militares (four plants)
Industrias Quimicas Argentinas Duperial SAIC
Sulfacid S.A.
Zarate Sulfurico S.A.

In addition to the small acid plant of Buenos Aires Gas Works, the 24,000 tonnes brimstone acid plant of the National Water Works was closed in 1959, but probably only temporarily. With the exception of two small plants, one of them a chamber plant, their capacities range from 66 to 110 tonnes per day all based on the contact process. Effective capacity is estimated to be little more than 150,000 tonnes. This is due in part to the limitations imposed on the by-product acid manufacturers who because of irregularities in deliveries of zinc blende are rarely able to operate their plants in excess of 80% capacity, and also because of the limitations of the Berisso plant of Fabricaciones Militares. Built in 1951 to manufacture sulphuric acid from acid sludges arising at oil refineries, technical difficulties prevented this plant from operating on this basis and it subsequently had to be modified to burn brimstone. Originally rated at 23,000 tonnes a year the highest output is reported to have been achieved in 1958 when 13,000 tonnes sulphuric acid was produced.

In 1959 and also in 1960 demand was comfortably met by available acid capacity and the very tight supply situation of 1958 has not recurred. In 1960 prolonged strikes in the metallurgical and rayon industries, both large acid users, severely affected acid suppliers which in several instances had to cease manufacturing. Consumption in 1960 is estimated at only 120,000 tonnes (100% H_2SO_4). It is thought, however, that increasing requirements in all sections of industry will necessitate substantial additions in the sulphuric acid sector and Duperial, under the company's major expansion programme of various chemical plant, is at present building a sulphuric acid plant at San Lorenzo with a daily capacity of 200 tonnes (100% H_2SO_4) and facilities to manufacture 65% oleum and battery acid.

Consumption by Industries — 1956

	% of total
Petroleum	28.0
Water treatment	21.6
Rayon and cellophane	12.6
Fermentation industries	2.0
Textile industries	1.5
Leather industries	0.7
Metallurgical industries	3.0
Batteries	1.6
Copper sulphate	0.8
Lithopone	3.9
Nitric acid	1.0
Tartaric acid	2.3
Activated earths	2.5
Vegetable oils, fats and soaps	2.0
Paper industries	1.5
Miscellaneous (fertilizers, explosives, chemicals, etc.)	15.0
	100.0%

Sulphuric Acid Consumption

The following table shows the distribution of sulphuric acid in the Argentine in 1956:—

Sulphuric Acid Consumption
('000 tonnes 100% H_2SO_4)

1950	83	1958	153
1955	105	1959	139
1956	122	1960	*120
1957	118	1961	*160

* Estimated.

The expansion of the viscose industry in the subsequent three years accounted for over two-thirds of the 30,000 tonne increase in sulphuric acid consumption.

Future Demand

Oil Refineries. Although the petroleum industry was the largest single sulphuric acid consumer up to 1958 with an annual requirement of approximately 40,000 to 45,000 tonnes sulphuric acid, the application of new refining techniques is not expected to result in any increase of sulphuric acid requirements commensurate with the greater throughput of crude oil.

Rayon and Cellulose. The three manufacturers in this sector of the industry—SNIAFA,

Ducilo and Reysol—consumed in 1959 approximately 35,000 tonnes sulphuric acid and by 1962 their consumption is expected to rise by at least 12,000 tonnes annually. SNIAFA, the only manufacturer of staple fibre in the Argentine, is expected to increase production capacity which in 1959 was fully employed from 16 to 36 tonnes a day by the construction of a new unit. In addition a rayon filament plant is to be installed with an initial capacity of 10 tonnes daily. The company also manufactures a modest quantity of Cellophane.

The largest manufacturer of Cellophane film is Ducilo. The company's operations are being expanded spectacularly from 115 tonnes per month in 1959 to about 300 tonnes per month by the middle of this year when the company's second unit is due to reach full capacity.

Detergents. Sulphuric acid demand in this sector, which is represented by five major manufacturers, is increasing rapidly. The largest producer, Cia. General d'Asphaltos, owned by Shell Oil Company, is expected to cease operations at Wilde by 1962 resulting in a reduction of about 500 tonnes a year of sulphuric acid use.

Simultaneously, however, the Shell Oil Company is expected to expand its sulphonating facilities to produce some 600 tons annually of dodecyl benzene; thus Shell and other major detergent manufacturers can be expected to increase their sulphuric acid demands by at least 1,300 tonnes a year by 1962 although up to 1,000 tonnes acid more may be used if the evident demand for detergents is to be met.

Cosmetic and medicinal oils. This is another sector of the Argentine chemical industry which is expected to increase its activities substantially within the next two years. Current demand represented by five small companies is about 1,700 tonnes sulphuric acid annually and their requirements (to rise by 30%-100%) are expected to reach 2,700 tonnes by 1962.

Other notable increases in sulphuric acid demand are expected in chemical products generally, battery acid and food treatment, whereas the leather, textiles and paper industries are not expected to show greater acid needs in the immediate future. As indicated above, the establishment of a major steel industry in Argentina is creating a major new market for sulphuric acid. This together with the anticipated establishment of motor car factories by a number of U.S. and European producers, is also expected to add to the short-term demand.

Non-acid uses

Carbon Disulphide. Manufacture of CS_2 has been established in the Argentine since 1920 when a plant was installed by the firm of Borzone and Margeno near Moreno. This plant, after a number of transfers, is now owned by Industrias Quimicas Argentinas Duperial. In addition there are three other producers: Luis Grassi Limited, Cia. Quimica Bunge and Born and Partenopea Argentina S.A., a subsidiary of the Williams Quimica group. In view of mounting demand by the rayon and Cellophane industries—current consumption is about 8,500 tonnes—and for carbon tetrachloride manufacture, output of CS_2 is rising steadily. In 1955 some 5,900 tonnes CS_2 was produced and used. By 1959 this had increased to 7,500 tonnes. It is estimated that in 1960 sulphur consumption in this sector totalled approximately 10,000 tonnes and may exceed 13,000 tonnes by 1962.

In addition to rayon and cellophane, which account for the bulk of CS_2 consumption, under 30 tonnes a day is consumed for various viscose articles, including sponges. Approximately 1,000 tonnes CS_2 is at present consumed in carbon tetrochloride manufacture by Cia. Electroclor. The main outlet for this production is in the manufacture of Freon which is at present produced by four companies, the largest being Ducilo with a Freon plant having a capacity of 250 tons a year. Demand for this product is expected to expand as the manufacture of aerosols, which is fairly recent in Argentina, is expected to rise. Duperial has started construction of a major CS_2 plant, based on the F.M.C. methane/liquid sulphur process, which is due to come on stream in 1962 when it will replace the existing plant at Gerli.

Pulp and Paper. Papelara Rio Parana S.A. has announced plans for a new installation to manufacture dissolving and ordinary sulphite pulp, thereby increasing the company's annual

capacity from 6,000 to 17,400 tonnes pulp. In the U.S. $5.3 million project, Mo och Domsjo, the leading Swedish pulp producer, is expected to participate to the extent of SKr. 1.5 million and to provide technical aid. Sulphur demand of this sector of industry will thus increase by about 1,100 to 1,200 tonnes annually.

Other non-acid uses. Rubber manufacture consumes some 1,000 tonnes annually and about 1,500 tonnes is used in the production of sulphur dioxide and sulphates, etc., respectively. The demand for agricultural sulphur is variable and recent surveys have failed to provide a balanced picture. Estimates of requirements for dusting and lime sulphur range from 500 to 4,000 tonnes annually though it is believed that the latter tonnage is unlikely to be reached as a regular level of consumption until the mid-1960's.

Outlook

The prospect of steady industrial growth of the Argentine is reflected by the anticipated increase in the requirements of sulphuric acid and other sulphur products. Sulphuric acid production is likely to rise to 200,000 tonnes annually by 1962 and to meet this new capacity is being installed. The limited sulphuric acid demand for the manufacture of fertilizers, however, imposes a severe brake on the growth of the sulphuric acid industry. It is now widely expected that the Argentine will have to use increasing quantities of fertilizers in order to raise food production, and to produce crops more economically. The main agricultural regions are in the north-east, the Chaco and Santiago del Estero and the extreme north-west. Crop yields are low and generally the eastern half of the country has a pronounced phosphate deficiency whereas in the west shortage of nitrogen is in evidence. Potash deficiency is most pronounced in irrigated areas. The need for a larger fertilizer use is evident and the recently announced nitrogen fertilizer project should go some way towards meeting it.

Estimate of Brimstone Consumption — 1960

Sulphuric acid	38,000
Carbon disulphide	9,000
Sugar	3,000
Liquid SO_2	1,500
Leather	1,000
Pulp and paper	2,000
Rubber	1,000
Sulphites, hypo sulphates and sulphates	1,500
Agriculture	2,000
	59,000

Other important sectors which may increase their sulphur and sulphuric acid requirements are pigments and phosphoric acid manufacture. Laporte Titanium Company has entered into an agreement with Titanit Cia Industrial de Pigmentos y Afines S.A. to render technical assistance in modernisation and extension of an existing small TiO_2 pigments plant. Albright and Wilson has completed similar arrangements with Villa Aufricht and Cia of Buenos Aires to manufacture phosphoric acid from phosphorus, but eventually wet process manufacture of phosphoric acid may be undertaken.

Despite the favourable consumption picture the Argentine is unlikely to make any significant additional demands on world sulphur supplies. On the contrary, the expansion of indigenous production of brimstone from native ores and of recovered brimstone should satisfy the rise in demand and, moreover, if demand rose sufficiently existing producers, notably Sominar, can be expected to implement expansion plans. Of particular interest to the domestic sulphur producers in this respect is the expansion of the sulphur market in the Mendoza province which is fact developing as a chemical centre. Its greater proximity to the sulphur mines makes it a more attractive market than that around Buenos Aires area. On current indications Argentine sulphur requirements should rise to over 80,000 tonnes by 1962 and by 1965, when fertilizer manufacture can be expected to have expanded substantially, the Argentine sulphur market is likely to grow to 125,000 tonnes.

Single Stage Leach Process for Zinc Concentrates

Sherritt Gordon's New Method

RECOVERY of zinc by roasting and leaching methods combined with electrolysis has been practiced since its commercial introduction in 1916. Where low-cost electrical energy is available the process has been used to treat zinc sulphide concentrates, which also contain appreciable amounts of lead, copper or iron sulphides. Economic recovery, however, is affected by (a) a high iron:zinc ratio in the concentrate which causes excessive formation of insoluble zinc ferrite during roasting resulting in low zinc recoveries, (b) efficient recovery of zinc requires a more or less complex two-stage countercurrent leach, and (c) the sulphur dioxide produced in roasting has to be disposed of in some way, and is usually converted to sulphuric acid.

When high iron-zinc ratios are encountered in zinc concentrate and when sulphuric acid production—the conventional way of utilizing sulphur dioxide evolved during roasting—is not considered economical, a process employing the following characteristics would have marked advantages:—

- very high extraction of zinc regardless of the iron or zinc content of the concentrate;
- use of a single stage leach in which no sulphur dioxide is produced;
- sulphur content of the zinc sulphide is recovered as elemental sulphur.

Such a process has been developed by Sherritt Gordon Mines Ltd., Fort Saskatchewan, Alberta.

The Sherritt Gordon Process

Briefly, the ground sulphidic concentrate is oxidized with air in sulphuric acid solution (recycled spent electrolyte at elevated temperature and pressure). During the oxidation about 75% of the sulphur is converted to its elemental form and can be recovered from the leach residue in its pure form by flotation, melting of the flotation concentrate, and hot filtration. The leach solution is subsequently purified, iron copper and cadmium being removed, and the zinc is recovered in a conventional electrolytic circuit. Extraction of the zinc is not affected by high iron content of the concentrate.

Investigations by F. A. Forward (Department of Mining and Metallurgy, University of British Columbia, Vancouver, B.C.), and H. Veltman (Research and Development Division, Sherritt Gordon Mines Ltd.) have shown that zinc sulphide can readily be oxidized quantitatively to ZN^{++} and S° in a solution containing sulphuric acid in sufficient amount to combine stoichiometrically with the zinc in ZnS without nitric acid being present. The necessary conditions for carrying out the reaction efficiently have been developed and

ZINC blende is material containing 51% Zn or more and as low an iron-zinc ratio as possible. The processing of this material entails in all instances calcining, the calcines being reduced to zinc metal by smelting, or increasingly, by electrolysis. The majority of calcining plants are equipped with by-product sulphuric acid installations to prevent SO_2 in roaster gases escaping to atmosphere.

The process outlined below has not so far found commercial application but it has certain advantages, notably the ability to make use of low-grade zinc ores which holds much promise for it. From the viewpoint of sulphur, its ability to reduce the metallic sulphide to elemental sulphur gives it more versatility than the orthodox process.

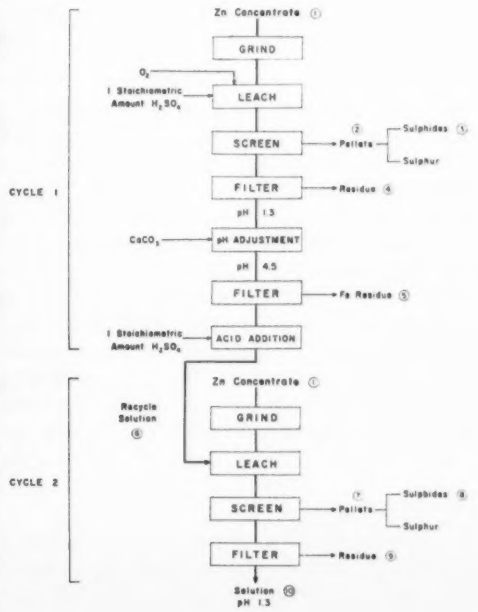
the principal elements of a cyclic process established.

Experimental Work

Commercial products having the following composition were studied:—

	Zn-Pb conc.	High Fe:Zn mixture	Pb conc.	Pyrrhotite conc.
Zn%	41.5	21.0	3.5	0.4
Pb%	7.8	4.4	65.5	0.4
Cu%	tr.	n.d.	tr.	n.d.
Fe%	10.0	32.0	11.2	50.5
S%	24.5	26.5	20.7	32.1
Insoluble material% ...	5.1	7.0	n.d.	12.6

In reaction tests zinc concentrate, usually 500 g., was charged as a water slurry to an open stainless steel autoclave with external gas heating, internal cooling coil and agitator and equipped with automatic controls for maintaining temperature within ±3°C. Sulphuric acid was then added in the required amount plus water to give a 14% pulp density, the autoclave closed, the agitator started and oxygen admitted to prevent sulphide formation during the start-up period. Temperature was raised to the required level and residual nitrogen from the air initially present purged by releasing the pressure momentarily. Oxygen was then admitted to give the required partial pressure.



In the test runs above the melting point of sulphur (119°C) the molten sulphur was found to form globules which melted and occluded unoxidized sulphides and solidified on cooling to form small pellets. If the last run was carried out below the melting point of sulphur, the elemental sulphur formed was finely divided. Two methods were used for separating the sulphur from the oxidized solids and leach solution: pelletizing and flotation.

Pelletizing. At the end of the leaching period the pulp temperature was raised to 140°C for 15 to 30 minutes to form molten sulphur globules. Pellets, formed on cooling below 100°C, were separated from the oxidized products and leach solution by screening on a 150-mesh screen. Oxidized solids—$Fe(OH)_3$ x H_2O, $PbSO_4$, CuO_2, etc.—were separated from the leach solution by filtration.

Flotation. At the end of the leaching period pulp was cooled to room temperature, filtered and the filter cake washed with water. The cake was then repulped with water to 15% solids and floated with a small amount of xanthate and pine oil to produce concentrate, middling and tailing, the latter comprising oxidized solids and insolubles.

Leaching Variables

Variables examined have included grinding time, temperature, O_2 partial pressure, sulphuric acid concentration, lime and zinc ion concentration.

Grinding. A light grind is required, but no advantage is gained by excessive grinding.

Temperature. It is found that if maximum dissolution of Zn is to be achieved, the reaction has to be carried out below the melting point of sulphur. The most suitable temperature is between 110° and 115° C.

Oxygen Pressure. Results at four hours at 20 p.s.i. O_2 are almost identical to those obtained in 1½ hours at 60 p.s.i. O_2. High O_2 pressure accelerates ZnS oxidation and conversion of Fe^{++} to Fe^{+++}.

H_2SO_4 Requirement. As PbS reacts more rapidly than ZnS, H_2SO_4 equivalent to the PbS present is added and enough additional H_2SO_4 is added to give the desired ratio for the ZnS. Data show a reasonably parallel relationship

between the stoichiometric amount of H_2SO_4 added and the amount of zinc dissolved.

Time. After 2 hour-leaching, zinc dissolution is over 90%, the iron in solution is reduced to less than 1.0 gpl, and the pH has reached a maximum of 1.3. The oxidized residue at no time contains more than 1% of the zinc.

Zn ion Concentration. Within the range examined zinc ion concentration has no adverse effect on leaching.

Sulphur Conversion. The amount of S° produced parallels the decomposition of ZnS as measured by zinc extraction thus substantiating:—

$$ZnS + H_2SO_4 + \tfrac{1}{2}O_2 \longrightarrow ZnSO_4 + S^\circ + H_2O$$

High Fe: Zn Ratio. Zinc loss in oxidized residue is less than 5%—a result that cannot be approached by conventional roasting and leaching methods for materials having the compositions mentioned above.

Results

At 110° to 115°C with the pH of the leaching solution below 2.0, the reaction

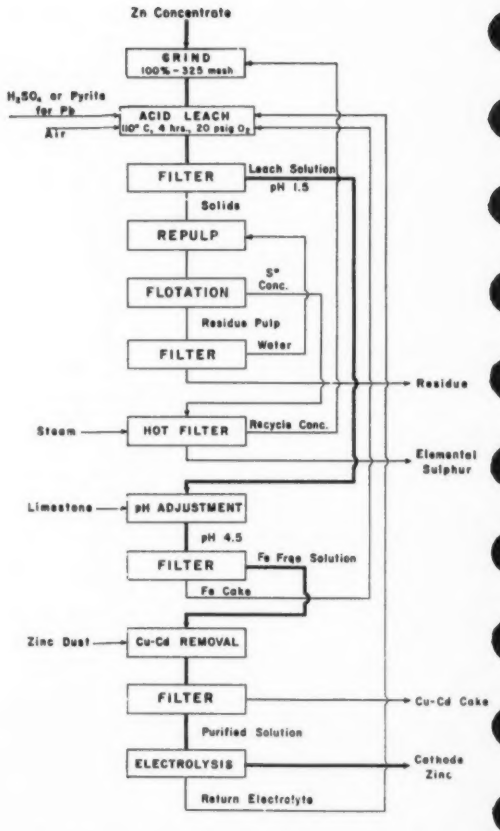
$$ZnS + H_2SO_4 + \tfrac{1}{2}O_2 \longrightarrow ZnSO_4 + S^\circ + H_2O$$

readily takes place, the extent of the reaction being primarily dependent on the amount of H_2SO_4 present in the reaction mixture. The rate depends on the surface area of the ZnS, the temperature (below the melting point of S°), and oxygen pressure, but does not appear to be markedly affected by the concentrations of Zn^{++} and SO_4^{--} ions in the leach solution. Substitution of some iron in the ZnS lattice does not adversely affect the progress of the reaction. PbS present (about 10%) reacts with H_2SO_4 at 110°C to produce $PbSO_4$ and S°.

$$PbS + H_2SO_4 + \tfrac{1}{2}O_2 \longrightarrow PbSO_4 + S^\circ + H_2O$$

A stoichiometric amount of H_2SO_4 for the lead present in zinc concentrate is also added therefore; it can be calculated from the PbS content of the concentrates. For high zinc concentrates, the H_2SO_4 content of the feed slurry may range from an H_2SO_4/ZnS + PbS molar ratio of 1.1/1 to 1.4/1.

The leach solutions produced in the investigations were substantially similar to those produced in conventional zinc leaching operations. $CaCO_3$ was added to increase the pH to about 4 to 4.5 to precipitate most of the dissolved iron. The behaviour of arsenic and



antimony, present in small amounts, has not been examined, nor has copper and cadmium removal been attempted. Any silver present is assumed to be precipitated in the course of Cu-Cd removal and the remainder in the oxidized residue.

Pellets and flotation concentrates have been heated to 400°C to remove S° by distillation or to 130°C to separate sulphur from sulphides by filtration, the residual sulphur being reground and returned to a subsequent leach. This sulphide product, primarily unreacted cores of original ZnS particles cooled with elemental sulphur, leached as readily as concentrate.

Conclusions

Sherritt Gordon Mines process makes it possible to treat a finely-ground zinc concentrate with a solution containing about 60 gm.

per litre Zn and 10 to 12% free H_2SO_4 by agitation in an autoclave at 110°C using an O_2 pressure of 20 p.s.i. to extract 99% of the Zn from a 40% Zn concentrate in 2 to 4 hours. Lead present is converted to $PbSO_4$ and with iron hydroxide and other insoluble oxides is separated as residue by filtration.

Sulphur present in ZnS can be quantitatively converted to S° as pellets or separated as a high-sulphur concentrate by flotation. This avoids, therefore, the necessity of producing sulphur dioxide or sulphuric acid in conjunction with an electrolytic zinc operation. Sulphur can be separated from the pellets or concentrate by hot filtration and the undissolved ZnS returned to the leach.

As the resulting solution has a pH of 1.0 to 1.5 and a Zn^{++} content of 120 gm. per litre or higher, it should be amenable to purification by electrolysis, thereby producing cathode zinc and regenerate H_2SO_4 for recycling to subsequent autoclave leaching operation.

Although H_2SO_4 required can be regenerated quantitatively by electrolysis, additional H_2SO_4 from outside sources is required to react with PbS. This small amount of acid can be added as manufactured acid produced from the sulphur liberated by the leaching reaction. The flowsheet shown below indicates a procedure for treating a zinc concentrate.

Autoclave design and techniques are well established for treating sulphite materials at 100 p.s.i.g. and 110°C using solutions at pH 1 to 2. Heat generated by the reaction should be sufficient to maintain the autoclave at the reaction temperature. The minimum economic size of the latter predicates the minimum economic capacity of the commercial facilities.

Extraction of zinc is unaffected by high iron content of the concentrate, which often prevents satisfactory zinc recovery due to formation of insoluble zinc ferrite during conventional roasting. Extraction has been found to be of the order of 98%. The direct pressure leach process is therefore distinctly advantageous when high iron-zinc ratios are encountered and when sulphuric acid production is not considered economical.

Cost Estimates

Capital cost of a plant for zinc recovery by direct pressure leach process is reported to be substantially the same as for conventional facilities (roasting, leaching, electro-winning and acid plant). For a plant of 220 tons a day capacity of zinc, direct operating costs of the conventional and the direct pressure leach processes are almost the same, subject to the local labour and utilities costs.

In particular, the direct pressure leach process offers credits for additional zinc recovery (approximately 5% when treating low-iron concentrates, more for high-iron materials) and for the elemental sulphur product, which are of the magnitude of 0.36 cents to 0.26 cents per lb. of zinc respectively. These figures must be compared with the conventional processes credits for the recovery of waste heat (approximately 0.19 cents/lb. Zn) and for the sulphuric acid produced (adjusted for its production costs) assuming that the latter can be sold at reasonable profit.

Q.V.F. GLASS PUMPS AND VALVES

IDEAL for the conveyance of corrosive liquids of water consistency, are two recently introduced glass pumps—Models GPA/6 and GPA/9—by Q.V.F. Ltd., Duke Street, Fenton, Stoke-on-Trent, Staffs., England.

Both pumps are of the centrifugal type running at medium speed. The glass impeller is of simple design based on a vortex-type inlet with specially designed arms.

The mechanical seal is a glass-loaded Fluon (polytetrafluoroethylene) bellows rotating on a glass plate and a specially-designed bearing chuck holds the precision ground impeller shaft.

A feature of these pumps is their freedom from corrosion. They are currently being used for sulphuric acid and for sulphuric acid mixed with nitrous oxides.

Maximum recommended working pressure is 50lb. p.s.i.

Occurrence of Sulphur Deficiency States in Brazilian Coffee Plantations

ANALYSES of Brazilian soils have indicated that a number of soil types show low levels of sulphur content. In view of the recent trends to heavier fertilization of coffee crops and the use of N, P and K fertilizers with low-sulphur values there is a greater possibility to-day of finding enhanced sulphur deficiency in coffee cultivation having to be remedied.

In 1952 Malavolta (1) gave results indicating that Brazilian soils contained low levels of sulphur and he predicted use of low-sulphur fertilizers might lead to deficiencies in field crops. Greenhouse studies by McClung *et al* (2) showed growth responses to added sulphur in several important Brazilian soils provided that adequate phosphorus is also supplied. Subsequently McClung and Quin (3) observed that where nitrogen fertilization was heavy, sulphur deficiency symptoms in grass became severe in the second year. More recently, Lott, McClung and Medcalf (4) have studied sulphur deficiency in coffee.

Sulphur Treatment Experiments

In the experiment, three levels of sulphur treatment were established, 10, 20, and 200lb. sulphur per 2 million lb. of soil* using calcium sulphate ($CaSO_4.2H_2O$) as the sulphur source. The soil (moisture content 20%) was turned to pH6.0 with equal parts of $MgCO_3$ and $Ca(OH)_2$. For each culture in an earthenware jar 30lb. soil was used. Base treatment was N, P and K at rate of 400, 300 and 265lb. per 2 million lb. of soil. In November 1957, each jar was planted with a young coffee tree (about 10 inches tall). During the subsequent growth period of 19 months, nitrogen was supplied at a rate of 100lb. per 2 million lb. of soil in September 1958 and again in February 1959, using ammonium nitrate.

Leaf samples were collected in December 1958, nitrogen, phosphorous, potassium and magnesium were determined by methods outlined by Lott *et al* (5). Calcium was determined by flame photometry with a Bechmann Model DU spectrophotometer. Total sulphur and easily reducible sulphur were determined by the method of Johnson and Nishita (6), (7) in which sulphur compounds were reduced to H_2S by digestion with a mixture of hypophosphorous, hydriodic and formic acids. The sulphide thus formed reacts with a precursor to form methylene blue which is measured in a colorimeter.

Chlorosis or Coffee Leaves

In late 1958 a chlorosis of coffee leaves occurred in Brazil plantations in plants grown in soil determined as sandy loam and classified as Bauru inferior. The only fertilizer applied to the plantations was Florida rock phosphate supplying 341lb. P_2O_5 an acre in late summer 1957, and 1958, in the form of superphosphate, 51lb. P_2O_5 an acre and 25lb. sulphur an acre. Nitrogen was supplied as urea in 1957 in three applications totalling 150lb. an acre N. In 1958 four applications of Calnitro (lime ammonium nitrate) were made supplying a total of 191lb. N an acre. A diagnosis of nitrogen deficiency was tentatively made but an application of Calnitro caused a worsening of the condition. Sulphur deficiency was the final diagnosis and gypsum was applied and four levels of treatment were used: 0,33,66 and 132 grammes $CaSO_4.2H_2O$ per tree, corresponding to 0,12,10 and 40lb. of sulphur an acre. Calnitro was applied again in April 1959 (268 grammes per tree) and again in July (same rate) and in September 1959 muriate of potash (100 grammes per tree). Leaf samples were taken in October 1959 for sulphur determination.

Benefits of Gypsum

In early 1959 the coffee trees appeared to have benefitted to some degree by the heavier applications of gypsum but by July 1959 chlorosis was again pronounced and leaf analyses for sulphate-sulphur gave values ranging from 100 to 340 p.p.m.

Results obtained show that chemical analysis of coffee leaves for sulphate-sulphur can be used effectively as a means of diagnosis

* Approx. equal to 1 acre to plough depth (about 6 inches), thus 1lb./2 million lb. is approx. equal to 1lb./acre.

of sulphur deficiency in conjunction with the less positive expedient of observing foliar symptoms.

Results

From the results indicated in the table below it is evident that applications of gypsum produced marked increases in leaf levels of sulphate. Plots receiving no gypsum gave a mean value of 126 p.p.m. as compared with 381, 724 and 784 p.p.m. for 10, 20 and 40lb. treatment. Plots without gypsum treatment gave values below the 200 p.p.m. level, believed to be the approximate borderline between deficiency and adequacy. Trees without gypsum applications averaged 40% chlorotic leaves while those treated with 20lb. and 40lb. sulphur an acre gave only 4 and 3% chlorotic leaves.

Sulphate-Sulphur in leaves of Coffee Fertilized with Gypsum

Sulphur applied (lb./acre)	Sulphate-Sulphur in Leaves (p.p.m.)				% of leaves chlorotic
	No mulch	Light mulch	Heavy mulch	Mean	
0	191	106	92	126	40
10	380	295	800	381	11
20	476	466	1,129	724	4
40	480	948	925	784	3
LSD(.05)	123	123	123	71	—

Levels of sulphate sulphur in the vicinity of 200 p.p.m. are considered near the borderline between deficiency and adequacy and the data tend to show that analysis for sulphate-sulphur affords more sensitive diagnosis than results for total sulphur.

Surveys of coffee plantations suggest that sulphur supplies are adequate in most plantations under current conditions of fertilizer practice with N, P and K. In São Paulo use of chemical fertilizers is in general less than moderate, and in Parana virtually nil. Use of considerable amounts of urea and the locally produced Calnitro, in lieu of ammonium sulphate can be expected to lead to deficiencies unless sulphur is supplied from other sources. Trial results have indicated that the small amounts of superphosphate have not sufficed for sulphur supply and repeated applications of gypsum at 40lb. an acre a year have not, as yet, proved to be completely adequate.

Sulphur Competition

Experience to date has not been lengthy enough to show what qualities of applied sulphur are adequate, but it is suggested by Lott *et al* (4) that applications may be needed more than once a year. At low levels of sulphur supply there may be competition for available sulphur between the coffee tree and micro organisms decomposing mulch material.

As yet, no trials with superphosphate containing added quantities of sulphur — as used on Australian grasslands—appear to have been carried out in connection with coffee.

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U.K. Brimstone Imports in First-Half of 1961 Highest on Record

CONSUMPTION of sulphur in all forms* during the first half of 1961 totalled about 525,000 tons, compared with 528,000 tons in the first half of 1960. Whereas sulphur consumption for sulphuric acid manufacture increased 1% to 475,000 tons, non-acid uses mainly due to reduced activities in the rayon industry declined 14% to 50,000 tons. Imported brimstone, pyrites and filter cake accounted for 77% of the total consumption* and indigenous sources of supply — recovered brimstone, sulphur in anhydrite used for sulphuric acid production, spent oxide, sulphur in zinc smelter gas, coal gas and ferrous sulphate—represented the balance (23%).

RAW MATERIALS

With the exception of brimstone—imported and recovered—consumption in the first half of this year of sulphurous raw materials for sulphuric acid manufacture was up to 11% lower than in the first half of 1960.

Anhydrite

Consumption of 373,705 tons anhydrite in the first half of this year was 2% lower than in the same period of 1960. Maintenance work on one of the kilns at the Billingham plant of I.C.I. is reported to have reduced throughput. The other two anhydrite acid producers—Solway Chemicals and United Sulphuric Acid Corporation—are reported to be operating at or near design capacity.

Spent Oxide

Consumption of 111,336 tons spent oxide was 10.7% lower than in the same period of 1960, mainly attributable to the declining trend of output from some of the smaller manufacturers producing acid for sale. Stocks of spent oxide held at consumers' works represent about 16 weeks' consumption.

Recovered And Other By-product Sulphur

Consumption for sulphuric acid manufacture of recovered brimstone, H_2S extracted at oil refineries, gasworks and coke ovens, filter cake, sludge acid and ferrous sulphate from pickling operations and titanium pigments production totalled 36,372 tons in the first half year, 16.9% more than in the same period of 1960. The increase is attributable mainly to increased use of ferrous sulphate and of H_2S, while that of recovered brimstone remained substantially unchanged. Recovery of brimstone at oil refineries has risen slightly, but operations based on extraction from spent oxide ceased at the end of 1960. Consumption of sulphur filter cake is estimated to have increased to 8,500 tons in the period January to June 1961 to meet the higher level of sulphuric acid production at Flixborough.

By-product Acid At Zinc Smelters

Use of sulphur in zinc smelter gases declined 4.7%, reflecting the modest decline in metallurgical operations at the Avonmouth and Swansea works of Imperial Smelting Corporation.

Pyrites

Consumption of pyrites in the first half of 1961 of 166,375 tons was 4.8% lower than in the same period of 1960. Consumers' stocks of pyrites decreased by about 4,000 tons since the beginning of this year, and at the end of June totalled 128,255 tons, about 20 weeks' consumption. Imports in the first half of 1960

Pyrites Imports, January - June

Origin	1961 Tons	Value per ton	1960 Tons	Value per ton
Cyprus	108,963	£4 8s. 2d.	96,783	£4 14s. 0d.
Spain	10,988	£4 1s. 10d.	5,427	£4 19s. 3d.
Sweden	13,815	£4 8s. 5d.	11,281	£4 10s. 6d.
Eire	—	—	1,816	£3 1s. 6d.

* Excluding sulphur in anhydrite used for direct manufacture of ammonium sulphate which is estimated at an annual rate of 190,000 tons S.

Brimstone Imports, January - June

Origin	1961 Tons	Value per ton	1960 Tons	Value per ton
U.S.A.	137,275	£10 0s. 0d.	168,088	£10 1s. 10d.
Mexico	48,808	£9 13s. 6d.	41,788	£10 0s. 8d.
France	79,616	£10 5s. 6d.	48,398	£10 12s. 6d.
Other	5	—	10	—
	265,704	—	**258,284**	—

totalled 130,766 tons, 13.2% more than in the same period of 1960. The principal supplier, accounting for 81.2% of imports, was the Cyprus Mines Corporation. Spain increased her share of the U.K. market from 4.7% to 8.2%, and Sweden from 9.8% to 10.5%. Eire did not supply this year.

Brimstone

Consumption of imported brimstone for sulphuric acid production in the first half of this year totalled 193,784 tons, 4.3% more than during January to June 1960, and the highest on record and reflecting the increased requirements of new brimstone acid plants. Consumption of imported regular (non-acid) brimstone declined about 6,000 tons. Brimstone imports rose to a new peak and at 265,708 tons were about 8,000 tons (3%) greater than during the first half of 1960. Their mean value of £10 0s. 3d. per ton compares with £10 9s. 6d. per ton in the first half of 1960.

Imports of U.S. Frasch sulphur declined 31,000 tonnes (18%) compared with the first half of 1960 and represented only 51.6% of total imports. Mexican Frasch sulphur supplies accounted for 18.4% of U.K. imports compared with 16.2% in the first half of 1960, while imports of French recovered sulphur rose steeply by over 31,000 tons (+65%) to account for 30% of U.K. imports (18.7%) in the first half of 1960). Consumer stocks in the first half year increased by 18,700 tons to 71,498 tons which represents about 10 weeks' consumption.

SULPHURIC ACID

Production

During the first six months of 1961 production of sulphuric acid totalled 1,346,823 tons (100% H_2SO_4), an increase of 9,900 tons (0.8%) compared with the first half of 1960. Whereas output in the first quarter of this year was fractionally lower than last year's, results for the second quarter show an increase of over 10,000 tons.

Of available capacity, which during the first half year was equivalent to 3.12 million tons (100% H_2SO_4) a year, about 86.5% was employed. In the second quarter available plant capacity rose 27,500 tons and employment declined to 83.9%. Contact acid plants contributed during the first half year 84.8% of the total output and the balance was produced in chamber and tower plants; in the first half of 1960 the production of contact acid was 83.7%.

Changes in the pattern of raw materials used in acid manufacture emphasise the steady increase in brimstone acid (see table below).

Consumption

Consumption of sulphuric acid has declined fractionally (0.3%) to 1,367,649 tons (100% H_2SO_4) including about 12,000 tons of reused acid. Acid consumption for fertilizer manufacture, in particular superphosphates (+8.4%), increased substantially and deter-

Raw Materials for Sulphuric Acid Manufacture

Sulphuric acid from:	Second Quarter 1961	First Quarter 1961	Average 1960	Second Quarter 1960
Imported brimstone	42.3%	41.9%	40.9%	40.1%
Recovered and by-product sulphur	7.3%	8.0%	6.9%	6.8%
Pyrites	16.1%	16.1%	17.0%	16.7%
Spent oxide	11.6%	12.5%	12.3%	12.5%
Anhydrite	17.3%	16.0%	16.9%	17.4%
Zinc concentrates	5.4%	5.5%	6.0%	6.5%
'000 tons—100% H_2SO_4	665	682	675	654

Consumption of Raw Materials for Sulphuric Acid Manufacture

	First half 1961	First half 1960	% Change	Second half 1960	% Change
Imported	193,784	185,809	+ 4.3	191,922	+ 1.0
Recovered, H_2S, filter cake, etc. ...	36,372	31,144	+16.9	34,423	+ 5.7
Pyrites	166,375	174,794	− 4.8	178,170	− 6.6
Spent oxide	111,336	124,751	−10.7	125,455	−11.2
Anhydrite	373,705	381,383	− 2.0	378,706	− 1.3
Zinc concentrates	95,584	100,275	− 4.7	97,246	− 1.7
Sulphur content	474,651	470,033	+ 1.0	479,895	− 1.1

Sulphuric Acid Consumption ('000 tons 100% H_2SO_4)

	First half 1961	% Change	First half 1960	% Change
Fertilizers	491	35.7	464	33.8
Superphosphates	**343**	**24.9**	**317**	**23.1**
Ammonium sulphate	**148**	**10.8**	**147**	**10.7**
Titanium dioxide	229	16.7	231	16.8
Rayon and transparent paper	121	8.9	143	10.4
Metallurgy	66	4.8	74	5.4
Soap, glycerine and detergents	64	4.7	63	4.6
Oil refineries	38	2.8	39	2.8
Dyes	51	3.7	54	3.9
Plastics	31	2.3	31	2.3
Miscellaneous	276	20.4	275	20.0
Total	**1,367**	**100.0**	**1,374**	**100.0**

gents modestly (+1.2%). Titanium oxide manufacture, hitherto an important growth industry, slightly (−1%) reduced its use of sulphuric acid, while more significant reductions of acid consumption were recorded in the rayon (−14.8%) and steel (−12%) industries.

Sulphuric Acid Exports

In July, nearly 1,000 tons of sulphuric acid (100% H_2SO_4) was shipped by Solway Chemicals Limited, a member of the Albright and Wilson Group, from its Whitehaven works to the Continent. This shipment was the first under a multi-thousand ton contract which the company has gained.*

Outlook

In view of the steady increase in sulphuric acid output reported during mid-summer, the output in 1961 is expected to total about 2.8 million tons (100% H_2SO_4), about 4% more than in 1960. The increased raw material requirements are being met predominantly by imported brimstone, and use of pyrites and of indigenous raw materials other than recovered brimstone, H_2S, etc., is likely to be lower than in 1960. Although construction of a new anhydrite unit which will augment acid output of Solway Chemicals at Whitehaven by 50,000 tons p.a. is advancing, it will not affect output until next year. On current indications the U.K. will import in 1961 some 250,000 tons pyrites and 550,000 tons brimstone.

Electrolytic Regeneration Process for H_2SO_4

CLAIMS TO a practical electrolytic method of regenerating sulphuric acid and caustic soda from waste sodium sulphate solutions obtained in viscose manufacturing plants are made by a research worker, Joszef Kerti of the University of Budapest. He reports that the process yields 40% sulphuric acid and 60% caustic soda together with by-product hydrogen and oxygen.

A mercury cell is used which removes the sodium as amalgam as soon as it is formed.

$$2Na_2SO_4 + 2H_2O \longrightarrow 4Na + 2H_2SO_4 + O_2$$

Current efficiency is over 90% and the sodium/mercury amalgam flows to a decomposition chamber where water is added.

$$2Na + 2H_2O \longrightarrow NaOH + H_2$$

The sulphuric acid of 40% strength obtained is suitable for use in viscose production. As yet, no economics of the process have been revealed and hence judgement on its potential value must necessarily be reserved.

* See page 29.

Alkali Inspectors' Report

Emission of Acid Mist in Waste Gases Still a Problem

THE main emission problem continues to be the presence of acid mist in waste gases from sulphuric acid manufacture, the *97th Annual Report on Alkali & C. Works* records. This is not a sulphur trioxide mist but a mist of sulphuric acid particles which apparently consist of nuclei of SO_3 with an envelope of molecules of water vapour around them. The physical state is such that the mist is almost unaffected by passage through standard absorption plant irrigated with liquids in which sulphuric acid is readily soluble.

Experiences with Mists

Inconsistencies between the experiences of different works are noted by the Alkali Inspector. Modifications of operational techniques giving decreased mist formation at one works may have the opposite effect at another. A special filter-type mist arrestor is giving satisfactory results on a production unit but applied to another unit on the same site and using the same raw materials has proved largely ineffective. If production is based on anhydrite, mist formation seems almost inevitable; when based on brimstone there may or may not be a mist problem.

There is no esoteric mystery, the Inspector records, but merely a lack of fundamental scientific knowledge. Mist is a very broad term and possibly no two mists are quite alike, differing in particle size and in the number and arrangement of the water molecules round the SO_3 nucleus. Some may contain small amounts of nitric acid derived from nitrogen in the air. Electric precipitation is the answer but is an expensive one as its successful application at some works had shown. Ceramic filters which have proved partly successful have been replaced by glass wool filters with appreciable success. Production of sulphuric acid in England and Wales in 1960 totalled 2,475,000 tons (100% H_2SO_4) compared with 2,213,000 tons in 1959 and 821,000 in 1938. The proportion of sulphuric acid made in 1960 by chamber and tower processes was 14.1% and by contact process 85.9%, compared with 60.3% and 39.7% in 1938. The report notes the increasing use of indigenous recovered raw materials as a source of sulphuric acid.

Tons 100% H_2SO_4

	1938	1946	1960
From anhydrite	62,000	100,000	457,000
From spent oxide ...	175,000	233,000	318,000
From recovered sulphur	nil	3,000	123,000
From hydrogen sulphide ...	5,000	7,000	19,000

It will be noted that 1960 acid production from native and recovered materials of 917,000 tons was greater than overall pre-war output, including brimstone and acid sludges from oil refining, ferrous sulphate from pickling iron, and from chemical processes.

Chamber and Tower Processes

The number of works registered has fallen over the year from 36 to 30. The number of individual plants concerned is 46. Production

Sulphuric Acid Production

Tons 100% H_2SO_4

	England and Wales			Scotland		
	1960	1959	1958	1960	1959	1958
Production	2,475,000	2,213,000	2,023,000	169,000	164,000	172,000
Proportion of plant in use (%) ...	89.4	82.1	80.1	78.4	75.7	74.8
Proportion made (%) in Chamber and Tower plant	14.1	14.4	19.0	28.8	31.5	36.6
in contact plant	85.9	85.6	81.0	71.2	68.5	63.4
Raw Materials Used (Tons)						
Pyrites	295,000	288,000	287,000	47,000	22,000	40,000
Sulphur, including H_2S and filter cake*	298,000	330,000	277,000	32,000	43,000	36,000
Spent oxide	239,000	212,000	231,000	8,000	7,000	9,000
Zinc concentrates	198,000	192,000	152,000	—	—	—
Anhydrite	760,000	748,000	749,000	—	—	—

* excluding recovered H_2S and filter cake in Scotland

amounted to 349,000 tons, compared with 318,000 tons in 1958.

Droplet emission can be dealt with by a relatively simple type of arrestor. Mist emission, however, seems to be confined to the two tower process plants and, it is suggested, may well be associated with the high nitrosity of the circulating acid. In one case the mist is satisfactorily dealt with by ceramic filters and in the other by electrical precipitation.

There were two infractions of the statutory limit of a total acidity in the exit gases of 4.0 grains per cu. ft. calculated as SO_3. In one case, escape of 5.3 grains, on a plant burning spent oxide, occurred during attempts to clear an obstruction in the final (third) Gay-Lussac tower. In another case, escape of 4.2 grains occurred on a pyrites burning unit due to a faulty temperature recorder.

Contact Processes

The number of works registered has increased from 41 to 43* and the number of individual plants at the end of the year, some being commissioned during the year, was 73, with a further 5 units being built.†

Acid Concentration

During the year 1960, the only operating example of a Gaillard tower concentrator was closed down.

Sulphide Works

The 128 registrations cover a great variety of operations practically all of which are serious potential offenders, notably the viscose rayon works which present the most difficult problems, or are likely to be of concern to the inspectorate for some years to come.

Carbon Disulphide

There are 49 registered plants for CS_2 but only five relate to manufacture. Remedies outlined last year have been carried out, but standard of plant maintenance and supervision are considered capable of further improvement. A still intractable problem relates to emission of SO_2 discharged at a relatively low level during the periodical charging of retorts.

Acid Sludge Works

Much of the sulphuric acid, some 9,000 tons yearly, used in the refining of coal tar or petroleum products remains on completion of these operations as an acid sludge which is malodorous. Where the amount is large the Alkali Inspector favours its use as a raw material for the manufacture of sulphuric acid by the contact process. An alternative is treatment with steam or water to give an impure dilute sulphuric acid, suitable for use in carbon operations and a pitch residue which can be burned or dumped. Choice of uses for the recovered sulphuric acid requires care, as its use in metal treatment has given rise to complaints.

Combustion of sludge acid is given reluctant provisional consent by the Alkali Inspectorate and discharge of gases has to be by high chimneys and with precautions to avoid emission of acid smuts.

Operations at one works (No. 657) have been abandoned as the storage of sludge caused local complaint. Stocks are therefore being dumped on the local authority refuse dump, treated with waste lime and sealed with incombustible material by bulldozer.

Shawinigan's CS_2 Process

SHAWINIGAN CHEMICALS LTD., Canada, has developed a process for the production of carbon disulphide using a fluidized bed technique. Carbon disulphide is produced by passing a gas comprising hydrogen sulphide up through a finely divided bed of carbon or silicon carbide particles which are thus formed into a fluidized bed, and is heated by passing current through it to maintain temperature 1,200° to 1,600°C. Carbon disulphide is formed and is recovered from the outgoing gases.

Carbon particles are preferably petroleum coke from a fluidized-bed petroleum coking process, rather than metallurgical coke or stoker coke. Contact time of the gas with the bed is 2 seconds for optimum results, a.c. or d.c. is used and open arcs are avoided. Several carbon electrodes can be arranged in the bed to provide even heating.

* New works registered were those of British Petroleum Ltd., Isle of Grain, and Cowburn and Cooper Ltd.
† Farmer's Company Ltd., Barton-on-Humber; Bradford City Sewage Works ,Bradford; Laporte Acids Ltd., Stallingborough; Fisons Ltd., Goole; F. W. Berk Ltd., Stratford.

Overcoming SO_2 Pollution Problems in the U.S.A.

Stauffer research on control techniques

AIR pollution problems associated with sulphuric acid plants in the Los Angeles area were discussed by two members of Stauffer Chemical Company, Richard V. Wallace and Lester H. Wittenberg, at a recent American Institute of Chemical Engineers meeting.

In the Los Angeles basin, Stauffer has four sulphur acid units. At the inception of the area's pollution regulations, these plants utilized converter systems in their three separate layers of vanadium pentoxide catalyst. The total volume of catalyst used was 180 litres per daily ton* of capacity in two of the plants where the raw material consisted of varying mixtures of sludge and sulphur and hydrogen sulphide; a third unit, a direct conversion unit in which brimstone was the raw material, was charged with 170 litres of catalyst per daily ton of capacity. Conversion efficiencies were 97% or less and the stack effluents contained 0.40% SO_2 required in the U.S. Government regulations. By adding as much catalyst as practicable in the light of pressure drop limitations, space velocity of gases was reduced, the SO_2/SO_3 equilibrium ratio adjusted and SO_2 concentrations reduced from 9.5% to 8% with the result that the amount of SO_2 in the tail gas was decreased by 50%.

Cost of Controlling Pollution

For about seven years the Stauffer plants were operated in this manner until plant expansions were required. Of $465,000 expended, it is estimated that at least $150,000 is attributed to Air Pollution Control District legislation on SO_2 emissions.

Addition of a fourth catalyst bed in the converters was necessary for efficient utilization of the increased quantity of vanadium pentoxide—now 220 litres per daily ton of capacity. Because of lower SO_2 content gases, the converter exchangers and flues had to be enlarged by 20% to maintain rates and produce acceptable pressure drops within the units.

Stack effluents from the four-layer converters contain 0.20% SO_2 or less at rated capacity and at lower operating rates, even less. Normally, conversion at rated capacity has been about 98.0 to 98.3% and the better (1.5%) use of raw material has helped partly to pay the cost of the projects.

Mist Emissions

A secondary problem for sulphuric acid producers under APCD legislation has been the limitation on visible plumes from effluent stacks. Emission was limited to a period or periods totalling three minutes in any one hour, to a Ringlemann Chart No. 2 reading or the equivalent to an opacity of 40%. The result of minute mist particles is that the mist ladings of 1 mg./ft.^{3} may be intolerable under conditions of high humidity, a dark sky or bright moonlight night. Despite proper operations, Stauffer still had intolerable plumes, and it became apparent that the greatly increased absorbing tower loadings which resulted from the low SO_2 gas strength required to meet the 0.20% SO_2 exit limitations, dictated the need for additional tower capacity. In 1947 the company started extensive expansion of absorbing towers at a cost of $49,000, which excluded the heavy costs involved in engineering plant shutdowns, start ups, and resultant production losses. Packed sections were enlarged, weir-type acid distributors, accurately and uniformly spaced, were installed and additional cooling area was added. Mist emissions then complied with APCD opacity regulations.

In 1949 additional H_2S from refineries was available to Stauffer and the stack emissions became troublesome. It was concluded that minute quantities of combined nitrogen and higher order hydrocarbons were passing through the sludge-burning equipment untouched, and were activated in the catalyst beds to form water vapour or compounds which combined with sulphur trioxide, and a visible mist resulted.

Research by the Stauffer engineering department proved that precipitation of the

* Short ton of 2,000lb.

strong acid mist was impractical, but that prehumidification of the gas was a satisfactory solution to the problem.

By 1950 a small single tube pilot precipitator was scaled up to what is believed to have been the first commercial electrostatic precipitator used specifically to clean up a sulphuric acid plant exit stack.

A second precipitator was installed at a different plant which utilizes the same principles as above but has minor structural modifications and a more modern rectifier for high voltage direct current in which automatic voltage control is incorporated in conjunction with a silicon rectifier. These stack precipitators have recovered at the most 18 tons of sulphur annually, although investment costs have been over $350,000.

Other Sources of Nuisance

Spent alkylation acid storage tanks which give off small quantities of very strong SO_2 are purged with a slipstream of stack gas. The cost of this system was $30,000, as a flame arrester, a low oxygen purge gas and an elaborate electrical anti-flash system were required to control the danger of flashback associated with the hydrocarbon content of the spent alkylation acid.

Operation of oleum plants has necessitated the use of a vent system on the storage tanks and loading racks. A complex coke-box and scrubbing system has been installed in one instance and in another case the sludge furnaces have been used to provide the blanket gas.

With the limitations imposed on SO_2 emissions, increasing quantities of sulphur have been recovered at oil refineries.

Sulphur Recovery
Long tons/year

Year				
1939	...	...	16,469	California Total
1948	...	...	23,559	Los Angeles only
1956	...	...	100,707	,, ,, ,,
1959	...	...	111,149	,, ,, ,,

Most of this recovered sulphur was converted to sulphuric acid.

Through more efficient techniques to control SO_2 emissions and in converting SO_2 to SO_3, Stauffer is reclaiming over 1,000 tons of sulphur annually. This quantity of sulphur represents, however, only 1% of the total sulphur released to atmosphere as SO_2. The $1 million spent on control of air pollution cannot be justified on the basis of raw material savings, although over the years the increased conversion will repay the cost. The stack investments, however, can never be offset in view of the insignificant quantity of sulphur recovered.

Titanium Dioxide Extraction By Continuous Process (Continued from Facing Page)

accurately assessed, but the pilot-plant studies have shown a one-third reduction in acid usage compared with conventional plants.

Plant Costs

Capital investment would also seem to be favourable. A 30,000 tons a year plant would cost $10 million or about $330 per annual ton of capacity. Capital costs for conventional plant are stated to range from $600 to $1,000 per annual ton depending on plant size, the higher cost being for the smaller plant.

Costs for Continental Titanium's new plant which will have a rated annual capacity of 6,600 s. tons a year, are expected to be about $400 per annual ton.

The claims of lower sulphuric acid requirements, labour and capital costs, are impressive and if proven in commercial scale operations the new process may find wide application in new titanium dioxide plants. The advantages claimed for the new process for savings foreseen by its ability to use ilmenite ore instead of slag with high (70%) TiO_2 content apply, however, only to local conditions and isolated instances in other parts of the world, e.g. Japan.

Although the steep expansion phase in the industry is now past new plants continue to be installed throughout the world. The most recent projects, all but one based on the sulphate route by the conventional batch process, will more than account for anticipated growth of demand by 1963. Thereafter, especially in underdeveloped and in Communist countries, further new constructions are likely, giving scope for the use of the new process.

Titanium Dioxide Extraction By Continuous Process

Soloducha-Continental Titanium method offers flexibility and economy

EXTRACTION of titanium dioxide by a continuous process invented by Nicholas Soloducha, vice-president of Continental Titanium Corporation which is now constructing a 20 short tons TiO_2 a day plant at Baie St. Paul, Quebec, Canada, offers promise of lower sulphuric acid consumption and greater flexibility and economy in operation than present batch processing. A pressure recycle is employed which utilises circuits of pipes (the subject of Canadian patent 610,334) instead of batch tanks of the conventional system.

Process Technique

In common with all TiO_2 plants, except those of Du Pont employing the chlorine route, the process, of which full details are still lacking because of pending patents, involves digestion of ilmenite ores in concentrated (93.19%) sulphuric acid*. Ilmenite ore is fed directly to the first processing stage with dilute sulphuric acid. Continental Titanium is planning to use 40 to 45% sulphuric acid, although it is possible to use acid of 25 to 55% strength. The ore-acid mixture is partially dissolved at about 490°F and 300 p.s.i.g. as sulphur dioxide is introduced to reduce ferric iron to ferrous. The resulting slurry is separated in self-cleaning thickeners and hydrocyclones to yield an intermediate solids concentrate with low iron (5% ferric oxide) and high titanium dioxide (over 80%) content.

No " Dead Spots " in Solutions

The concentrate is then mixed with more sulphuric acid until it is completely dissolved into ferrous and titanium sulphates. This step is also carried out in circuits of steam-jacketed pipes arranged with multiple circulating pumps and by-passes to prevent " dead spots " where solids could settle out of the circulating solutions.

Initial rapid hydrolysis of titanium sulphate is avoided in the Soloducha process by injection of the feed for the hydrolysis step directly into a circulating volume of solution which has been partially hydrolyzed. The feed is heated rapidly to the reaction temperature (185-190°F), the presence of free sulphuric acid preventing unwanted reactions.

Following the hydrolysis which takes about one hour the solution formed is injected into a hydrolyzed mixture circulating at about 140°F and after quick cooling, crystals of the preferred size are formed and are filtered off.

Independent Evaluation of Process

The pipe-circuit design was successfully tested in a pilot plant. To secure capital for a full-scale plant Continental Titanium submitted the process for independent evaluation by P. L. Bruyn of Massachusetts Institute of Technology who reported that cost of pigment production could be reduced by 20% to 30% according to the size of the plant.

Reasons he advanced for the reduced cost are as follows:—

(a) Cheaper raw materials such as ilmenite ores assaying about 43% TiO_2 and 51% Fe_2O_3 can be used without beneficiation to yield a 99.9% plus titanium dioxide pigment.

(b) Treated ores and slags represent an intermediate cost to producers of $45 to $60 a ton, whereas prior to the leaching step in the new process treatment costs of ilmenite ores are estimated at about $13 a ton.

(c) Sulphuric acid consumption is lower as cheaper dilute strength can be used for dissolution of the ore, and some of the acid liberated during hydrolysis can be recycled.

(d) As continuous processing can be carried out labour costs are reduced.

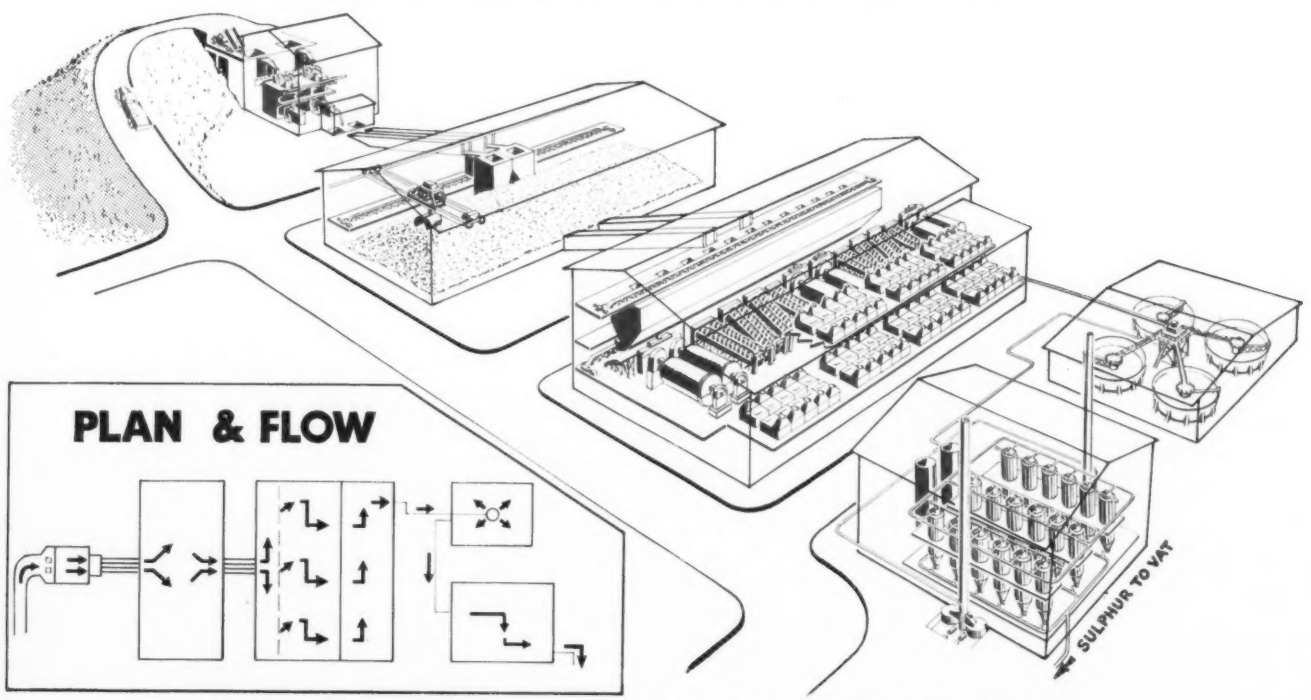
(e) Engineering estimates have shown that capital costs may be up to 30% less, depending on the plant size, than conventional plant.

Until the commercial scale plant which Continental Titanium is building at Baie St. Paul, Quebec, is in full operation—later this year—sulphuric acid consumption cannot be

(Continued on previous page)

* Sulphur 28, May 1960, page two.

Rozdolski Sulphur Ore Treatment Plant



Sulphur ore from the adjacent deposit enters the ore crushing plant (*far left*) **then passes to the storage shed, ball mill section thickeners** (*top right*) **and autoclaves** (*bottom right*).

— Copyright British Sulphur Corporation Limited

Sulphur Ore Treatment at the Rozdolski Plant

U.S.S.R. brimstone production now 1·4 m. tonnes

IN the last five years considerable efforts have been made in the U.S.S.R. to develop sulphur and sulphuric production facilities in order to keep pace with the requirements of the fertilizer and chemical industries. Expansion of brimstone production in particular from native sulphur ore deposits has been marked, and in 1960 it is estimated to have accounted for all but about 15% of total U.S.S.R. brimstone output of 1.4 million tonnes. Output originates from four production centres :—

(1) The Rozdolski Sulphur Works, near Lvov, in the Ukraine

(2) Kara-Tau, in Kazakhstan

(3) Gaurdak, in south-east Turkmenistan

(4) Aleksejevka (Shor-Su), near Kuybyshevo, in Kazakhstan.

The Rozdolski plant has an annual capacity of 650,000 tonnes high-purity brimstone; the Kara-Tau plant is stated to have a slightly larger capacity, but the other two works are small, probably less than 50,000 tonnes per annum each.

Opencast Mining

The flowsheets at these plants are similar, but plant modifications are embodied at the newer installations, of which Rozdolski is the most up-to-date. At least two further major plants are reported to be under construction. Native sulphur ores are mined in all instances by opencast methods, transported to the plant, subjected to flotation and subsequent autoclaving of the sulphur concentrate to yield high purity (99.8 to 99.9%) brimstone.

Ore Treatment

The Rozdolski Sulphur Works is near a large deposit representing an extension of the sulphur field in south-east Poland, and is stated to contain 20 million tonnes of ore of 25% to 30% S, 60% $CaCO_3$, $MgCO_3$ and SiO_2 and 10% clay. Mining started in 1954 and it is estimated that about 2½ million tonnes of ore are mined annually. The ore is transported in 25-tonne lorries to the plant and fed to the crushing section. At the first stage it is crushed from 900 mm. to 150-250 mm., and in the second grinding stage 20 mm. The ore then passes to a covered storage shed which holds 4,000 tonnes—the quantity required for one shift—as the plant throughout is approximately 550 tonnes an hour of ore. The plant operates on three shifts of 24 hours throughout the year, except for 20 days set aside for maintenance and repairs.

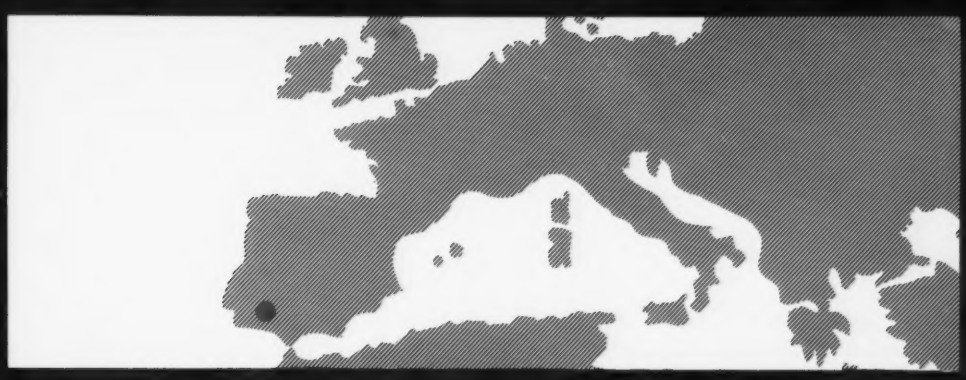
Two Autoclave Sections

From the storage shed ore is moved to a ball mill section where it is ground to 0.2 to 0.15 mm., passing through a classifier in closed circuit. The finely divided ore is mixed with kerosene and a small quantity of caustic potash as flotation reagents. The sulphur concentrate containing about 80% S then passes to thickeners and the dewatered concentrate is melted in autoclaves, of which at the Rozdolski Works there are two sections of 18 autoclaves each with a capacity of 50 cu. m. Melting is effected at 3 atm. pressure, using steam generated in a plant attached to the autoclave section. Impurities, notably bitumen and ash, rise to the surface of the molten sulphur which is drawn off from the bottom of the autoclave. At at least one other plant the molten sulphur is filtered, the filter cake containing about 45% S, which is supplied as raw material for sulphuric acid manufacture.

U.S.S.R. Brimstone and Acid Output

Of the brimstone output of 1.4 million tonnes in 1960 about 1 million tonnes was used in sulphuric acid production, accounting for one-half of total U.S.S.R. acid output, and about 350,000 tonnes was consumed by non-acid industries, notably pulp, textiles, rubber and agriculture. When completed, the two major plants now under construction can be expected to double U.S.S.R. sulphur output by 1963.

Pyrites...



COMPAÑIA ESPAÑOLA de MINAS de RIO TINTO S.A.

THE THARSIS SULPHUR AND COPPER CO. LTD.

Pyrites is a stable, assured and competitive source of sulphur. The Tharsis and Rio Tinto mines in Spain have supplied pyrites for over eighty years. Their known reserves are unrivalled.

← Aerial view of El Valle, one of the Company's villages at Rio Tinto. In the distance, Corta Atalaya.

...Europe's principal source of sulphur

Growth of World Sulphur Consumption Temporarily Halted

DURING the first half of 1961 the world consumption of sulphur in all forms failed to maintain the momentum of growth which had advanced Free World sulphur uses in 1960 by 6% to 18.4* million tonnes. The main contributory factor was the reduction of sulphur demand in the U.S.A. where, it is estimated, it was about 2 to 3% lower than in the preceding year. In Europe the first six months of 1961 were a period of consolidation after the spectacular results achieved in 1960. In the U.K. and in West Germany, the two largest consumers in Western Europe, and in most other countries there was practically no change in overall demand, but in Scandinavia and in Spain consumption appears to have risen slightly.

Expansion in Japan

The outstanding feature in the world pattern of demand is the continued expansion in Japan where acid and non-acid uses are estimated to have risen 6%. Despite substantially reduced requirements for ammonium sulphate production, requirements of other sectors, notably synthetic fibres, plastics and detergents, are outrunning available production capacity and it is expected that by 1962 Japan will have to produce 5 million tonnes (100% H_2SO_4) sulphuric acid to satisfy industrial needs.

In the rest of the Free World, which accounts for only 10.5% of total sulphur use, consumption increased, notably in South America, India and Far Eastern countries, whereas in Africa and in Australia and New Zealand the increase was modest.

U.S.S.R. Not Maintaining Acid Growth Rate

Communist countries, and in particular the U.S.S.R., are unable to maintain the high rates of expansion of sulphuric acid output evident in recent years. In the U.S.S.R. results for the first half year indicate a rate of growth of just under 5% and in several Eastern European countries results failed to meet plant requirements, notably in East Germany and Czechoslovakia.

In contrast to the stagnation of demand, albeit temporary, world production capacity continues to grow rapidly. To avert stock accumulation the major Frasch sulphur producers and, of course, the European pyrites miners, continue to pursue conservative production policies in aligning their level of operations to that of shipments.

The greater part of the impact on markets mainly in Europe, of the new production of French recovered sulphur has been absorbed as a result of the substantial growth of brimstone demand. This year's production, expected to total 1.05 million tonnes, is readily being taken into consumption and to augment stocks to a desirable level. In 1962 S.N.P.A. plans to produce 1.35 million tonnes brimstone and an adjustment of the supply pattern in Europe is likely to result.

Supplies from Canada and U.S.S.R.

More far-reaching changes are imminent as the result of growing production of Canadian recovered sulphur, of which the first export shipments are being made to Far Eastern markets and which is progressively filling the North Western and Californian sulphur markets of U.S.A. and gradually moving towards the Great Lakes market. Another factor in the world supply pattern is the growing supply potential of brimstone and pyrites from Communist countries. The current level of brimstone production in the U.S.S.R. of 1.4 million tonnes appears to provide a modest export surplus of up to 100,000 tonnes, which is likely to grow as plans for increased production mature. At present offers as far apart as Western Europe, India and Brazil are in evidence, and in the latter market, China also

* Including sulphur contained in sludge acid and by-product ammonium sulphate.

has appeared as a potential seller. Poland can be expected to make an impact on world brimstone markets after 1963, while sales of U.S.S.R. pyrites in Italy and offers elsewhere in Western Europe are already of some significance.*

PRICES

World Price

During the remainder of this year the level of world prices can be expected to remain stable, while the prospect for 1962 will be determined by the price policy of Canadian brimstone suppliers and European pyrites producers. The latter are known to be determined to secure a greater share of the market and may to this end embark on a more aggressive price policy, although an obvious limitation to the level of sales is the availability of pyrites roasting capacity. The possible rewards will have to be weighed against the likelihood of a return to instability of conditions in world sulphur markets, on which the volume of offers of brimstone and pyrites from Communist countries and the prospect of large-scale shipments from Canada is beginning to have an effect.

Frasch Sulphur

U.S.A. Prices posted by U.S. Frasch sulphur producers remain unchanged at $25 per ton f.a.s. U.S. Gulf ports for bright sulphur with discounts of $1 per ton for off-colour sulphur and of $1.50 per ton for delivery f.o.r. *ex*-mine. Whereas posted prices still only apply in a limited number of protected markets and the bulk of domestic and export shipments is based on delivered prices embodying freight contributions or other discounts of up to $3.50 per ton, the industry's price structure appears to be undergoing some changes under the influence of the growing volume of liquid sulphur deliveries and sales based on the individual companies' distribution points.

For some time the large and progressively mounting volume of brimstone recovered by oil refineries and natural gas cleaning plants has been sold locally at prices which are deemed economic from the operators' viewpoint and are not necessarily related to the competitive level of Frasch sulphur prices in the area. In the past year Texas Gulf Sulphur Company and Jefferson Lake Sulphur Company have been fulfilling the requirements of many customers in the North-Western U.S.A. which had previously been supplied from the Gulf, by deliveries from their brimstone recovery plants in Western Canada and the rising level of liquid sulphur deliveries from focal distribution points along the Mississippi and the Atlantic seaboard contributes to the trend of establishing price levels for individual consuming areas.

Currently along the Gulf of Mexico and in Florida (Tampa area) prices range from $25 to $27 and similarly in the "up-river" area along the Mississippi. In the North Central States and Great Lakes area which receives the bulk of supplies by way of transfer points on the Mississippi and only to a small extent by direct ocean shipments by way of the St. Lawrence Seaway prices range from $26 to $27.50 and along the Atlantic Seaboard around $26.50.

The improved methods of shipment and distribution on which all major producers are expending large capital sums can be expected to contribute to price stability and benefit particularly areas east and west of the Mississippi which have been supplied mostly by long rail hauls and which may now be shortened. The effect of price increases which are intended to raise f.o.b./f.a.s. Gulf ports equivalent returns to the Frasch Sulphur producers to $23 to $24 is reported to be slow but the producers resolve to achieve returns equivalent to the posted level of $25 remains unaltered.

Mexico. Posted prices for export to U.S.A. and abroad remain at $23.50 per ton f.o.b. Coatzacoalcos for acid treated bright sulphur and $22.50 for off-colour material. Although the current level of prices is higher than one year ago following the increase announced last December, effective returns are still below the level of posted prices.

Export Prices

The slower expansion of brimstone demand this year compared with the exceptional results of 1960, coupled with strong

* Under these conditions price stability, especially in Europe, is of even greater importance since any significant increase in the delivered cost of sulphur could induce major purchasers to examine new sources of supply more favourably and at the same time result in either realisation of potential sulphur recovery projects so that the sales volume from established sources of supply would be adversely affected.

competitive pressure from pyrites, appears to have put a brake on the major suppliers' efforts to raise the level of prices. In Western and Northern Europe delivered prices of U.S. and Mexican Frasch sulphur and of French recovered sulphur range from $26.50 to $31 per tonne c. & f. The differential between the Sulexco sales price to West Germany and Switzerland compared with that to other consumers in Western Europe, which resulted from the revaluation of the Deutsche Mark earlier this year, has been removed by reducing the landed price at Rotterdam by DM 3 per tonne.

Prices in general are at present stable and the offers of Russian and to a lesser extent of Polish sulphur at substantially lower prices equivalent to $22.50 to $24.50 per tonne c. & f. have not so far affected the tone of the market. Offers of Russian sulphur outside Europe are also up to $4 below the landed prices of established suppliers.

In India delivered prices for U.S. and Mexican sulphur and of French recovered sulphur range from $31 to $34 per tonne c. & f. In South America, notably Brazil and Argentina, delivered prices of U.S. Frasch sulphur are $32 to $33 per ton, representing an attractive return in the light of the prevailing cost of ocean freight.

In Taiwan, Canadian recovered sulphur is reported to have been landed at about $28 to $29 per ton, compared with the prevailing level of established U.S. Frasch sulphur supplies of $32. No firm quotations for Canadian supplies are as yet reported from other Far Eastern markets.

Recovered Sulphur

There has been no change in the price level of indigenous recovered sulphur supplies in Western Europe. In West Germany prices in the Ruhr and at Hamburg of brimstone recovered at oil refineries and by Ruhrgas AG. range from DM 118 to DM 125 per tonne, plus turnover tax, landing and service charges. In Holland recovered sulphur is sold at Dfl. 99 to Dfl. 104. In France delivered prices to domestic consumers range from NF 130 to 140 per tonne. In Sweden brimstone recovered by Svenska Skifferolje A.B. is sold at Skr. 158 to 160, supplies in liquid form attracting a small premium. Imported Orkla Sulphur is delivered at Skt. 158 per tonne. In the U.K. supplies of recovered sulphur from oil refineries delivered in liquid form attract a small premium compared with imported lump sulphur delivered at "pool prices."

The reduction by 22.2% of rail rates for sulphur in Western Canada has improved *ex*-works returns of suppliers on exports. Nomi-

Sulphuric acid plant of Compania Espanola de Petroleo S.A. Spain

nal *ex*-work prices remain at $23.50 per short ton, but actual returns are substantially lower varying in accordance with individual destinations.

Pyrites

The price level of European pyrites to be delivered during the second half of 1961 has remained substantially unchanged. Spanish crude fines continue to determine the general price level, Rio Tinto crude fines being priced at 60s. basis 48% S f.o.b. Huelva and Tharsis crude fines pyrites at 61s.; other Spanish pyrites except for a number of small producers supplying low grade pyrites who are quoting up to 12s. per tonne less are priced correspondingly within narrow limits. Rio Tinto confines gravity concentrates are quoted at 50s. Portuguese pyrites are based on 58s. per tonne f.o.b. Setubal basis 48% S a reduction of 2s. per tonne, and Cypriot and Norwegian pyrites are priced competitively. The average export value for Cypriot iron pyrites during the period January-April 1961 was 59s. 9d. per ton. Offers of Russian pyrites have been made in the U.K. and West Germany at prices ranging from 62s. to 68s. per tonnes c. & f., and a major sale to Italy has been reported.

Residues values remain firm on the Continent as well as in the U.K. Current quotation indicate 75s. per tonne for cupreous residues and 70s. per tonne for non-cupreous residues free Ruhr.

SUPPLY

U.S.A.

Production of Frasch sulphur which during the first half-year had been restricted to accord with the depressed level of demand, appears to be increasing slightly and is likely to average 440,000 tons monthly during the second half-year domestic consumption of sulphur in all forms, which is increasingly met by recovered sulphur and imported supplies, is expected to total about 3.2 million tons, representing a 10% increase compared with the first half-year. Exports, which during the first four months of 1961 were 13.7% lower than in 1960, improved during May and June and the first half-year's exports, excluding those to Canada, were about 2% greater than in the same period of 1960. Frasch sulphur stocks increased slightly during the first half-year to 3.7 to 3.8 million tons and are likely to be maintained at this level.

Mexico

Production of Frasch sulphur in the first half-year totalled 532,000 tons, about 2% more than in the same period of 1960. The increase is wholly attributable to the activities of Central Minera S.A., whose output in this period totalled about 15,000 tonnes. Exports totalled 549,300 tonnes, a decrease of 12.4% compared with the first half of 1960 and domestic sales also are lower by a similar margin. Frasch sulphur stocks, although slightly lower than at the start of the year, still exceed 1 million tons of which, however, more than one-third is represented by stocks of off-colour sulphur produced by Texas Gulf Sulphur Company and held in vat at Nopalapa.

Japan

The mining department of the Ministry of Trade and Industry is reported to anticipate difficulties in maintaining the present quota restrictions on brimstone imports in view of the expected GATT advice to Japan to free trade. The Japanese brimstone producers, who have been asked by the Ministry to reply to a detailed questionnaire on production costs, rationalisation measures and their ability to compete if brimstone imports were liberalised, are opposed to any Government measures which would remove the present protection of their industry.

U.S.S.R.

Production of brimstone is currently at an annual rate of 1.4 million tonnes. It is primarily based on the operations of four native sulphur ore refining plants and includes output of recovered sulphur from oil refineries, gas works and pyrite smelting totalling about 200,000 tonnes.

Poland

Production at the Tarnobrzeg sulphur combine is reported to be progressing according to plan and this year an output of 114,000 tonnes is foreseen. Whereas during the development stages last year it had been envisaged that a newly-developed "battery" process would be employed which would reduce the

need for crushing of run-of-mine ore and result in savings in operation costs, current production is based on conventional ore preparation, flotation and melting and filtering of concentrates containing 80-85% S. Output of 99.5% S sulphur and of filter cake containing 45% S results in recovery of about 90% of the sulphur content of the ore.

Czechoslovakia

In 1960 imports of brimstone are reported to have totalled 75,000 tonnes, compared with 59,000 tonnes brimstone in 1959. Contracted deliveries from Poland are expected to raise brimstone imports in 1961 to 95,000 tonnes.

RECOVERED SULPHUR

U.S.A.

Output reached a peak of 75,054 tons in April and the average rate of operation indicates that in 1961 production and deliveries will reach at least 820,000 tons, about 100,000 tons more than in 1960.

Canada

Output of recovered sulphur in Alberta and British Columbia during the first five months of 1961 totalled about 215,000 short tons, of which about 130,000 was delivered to consumers in Canada and North-West United States. The rate of production, which had risen to about 45,000 s. tons per month, is increasing slowly. Stocks at the end of May are estimated at 520,000 s. tons.

West Germany

Plans to utilise sour natural gas resources in North-West Germany include provision for the installation of H_2S extraction and sulphur recovery capacity by Wintershall AG. and Mobil Oil Company and associates. The additions to West German recovered sulphur capacity of up to 70,000 tonnes a year are expected to raise annual output to over 125,000 tonnes a year after the end of 1962.

France

Production of recovered sulphur by SNPA during the first six months of this year totalled 532,082 tonnes. Although the fifth and last unit has now been brought into operation, it is not yet working to capacity and routine maintenance has in recent months caused output from the third unit to be reduced. The present monthly level of output is about 95,000 tonnes brimstone. Deliveries during the first half-year totalled 452,733 tonnes, of which 267,409 tonnes was exported. Deliveries to the home market were at annual rate of 370,000 tonnes, slightly in excess of expectations.

PYRITES

The level of European pyrites trade, although lower than in 1960, has been well maintained in relation to sulphur demand as a whole. The decline is partly attributable to the exceptionally heavy volume of shipments, notably to West Germany, in January, 1960, but also to the evident levelling-out of demand and of sulphuric acid production.

Spain

Production of iron and cupreous pyrites during the first five months of 1961 totalled 948,500 tonnes, about 9% more than in the same period of 1960, in view of increased domestic requirements coupled with satisfactory export demand.

Cyprus

Exports of iron pyrites during January to April totalled 265,146 tons, 4% more than in the corresponding period of last year. Cupreous pyrites exports totalling 45,772 tons were, however, 55% lower.

Development plans of Cyprus Sulphur and Copper Company are progressing satisfactorily and the start of production of pyrites and copper flotation concentrates is imminent. Initially output at an annual rate of 30,000 tons pyrites concentrates is envisaged.

Czechoslovakia

Pyrites imports in 1960 totalled 50,000 tonnes, 2% less than in the preceding year.

West Germany

Production of pyrites, represented chiefly by the output of the Meggen mine, totalled 132,400 tonnes in the first quarter of this year, 3.8% less than in the first quarter of 1960.

France

Production of pyrites during the first five months of the year totalled 117,400 tonnes, 6.8% less than in the same period of 1960.

PLANT DEVELOPMENTS

Indonesia

Plans have been announced by the Government to extend the sulphuric acid plant at Sepandjang, Java, at a cost of $1.1 million by the installation of additional production and service facilities. Hitherto the bulk of installed capacity has been part of oil refining installations. In addition to the above expansion a 35,000 tonnes a year acid plant is being built in conjunction with the 100,000 tonnes a year superphosphate plant in Borneo now under construction by Soviet technicians.

Yugoslavia

Commissioning trials are in progress at the twin 900 tonnes a day (60° Bé) by-product sulphuric acid plant at Bor, which is based on copper smelter gases. Built by Hugo Petersen of Wiesbaden the converter section has special provisions to compensate for the variable SO_2 content of the feed gases. Sulphuric acid output in Yugoslavia totalled 145,500 tonnes (100% H_2SO_4) in 1960, 5% more than in 1959.

East Germany

The anhydrite acid plant at Coswig is coming on stream on 1 September. The rated capacity of 200,000 tonnes a year (100% H_2SO_4) is expected to be boosted by enriching the anhydrite feed with elemental sulphur. Acid production in East Germany in 1960 totalled 730,000 tonnes (100% H_2SO_4), 6% more than in 1959, but supplies remain short, especially as caprolactam output at Leuna is to be raised and titanium oxide manufacture is to be substantially increased, the latter to make East Germany independent of imports from the West.

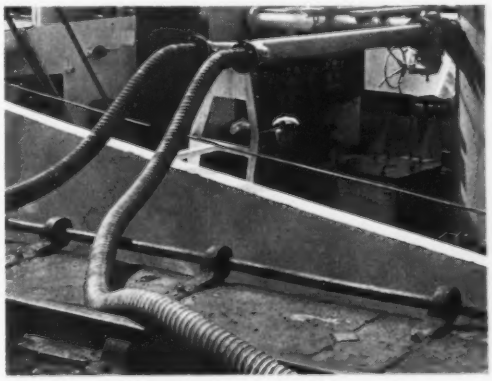
Canada

During July, the Electric Reduction Company's multi-million dollar plant at Port Maitland, Ontario, started production of phosphoric acid and triple superphosphate, and in August the dicalcium phosphate plant came into operation. Sulphuric acid requirements are being met by the Sherbrooke Metallurgical Company in the form of by-product smelter acid.

Freights

Reducing Sea-transport Costs by Grouping Sales

Low prices and keen competition, especially since the advent of more than plentiful supplies of "recovered" sulphur, have led producers to seek other means than cutting f.o.b. prices to make their material more attractive to potential consumers. An obvious line of attack was to find means of reducing sea-transport costs, which even on a depressed freight market, added as much as one-third to the price of the material on Transatlantic voyages. Frasch sulphur producers in the Gulf of Mexico have been able to effect big freight savings by grouping sales to a number of customers, none of whom could take more than 5,000 to 10,000 tons at a time, into single shiploads sufficient to fill a 20,000 tons bulk-carrier. Because of lower operating costs these large vessels can, and do, accept freights from $1 to $1.50 a ton less than conventional tramps of half their tonnage. With improving conditions for world shipping this differential is likely to widen as call grows for the smaller vessels. Bulk shipment also facilitates the establishment of



Export of 1,000 tons of sulphuric acid from Solway Chemicals Limited at Whitehaven to Europe **(See Page 14)**

stockpiles at major Continental ports from which small users who only want a few hundred tons at a time can be supplied. Recent charterings of bulk-carriers from the U.S. Gulf to near Continent have been made at the net equivalent of 29s. a ton — not significantly more than 25s. payable for a 1,000 tons coaster from Bayonne to Hamburg.

Appeal of Molten Sulphur

The other big effort to increase consumer-appeal which the U.S. and Mexican producers have made, although not so far on this side of the Atlantic, is of course, shipment by converted tankers and final delivery to users' works, of sulphur free from exterior contamination and in molten form ready for immediate use, with the consequent saving of the usual re-melting costs incurred with the customary solid material.

Moulded Sulphur Ship Forms

These successes in improved marketing and reduction of freight costs have also prompted some flights of fancy aimed at a similar objective. One such which has received a considerable amount of attention in European shipping and technical journals, was the subject of investigation by the Southwest Research Institute* of San Antonio, Texas. It provides for casting molten sulphur at the ports of origin, into ship forms and then towing them, semi-submerged, across the Atlantic to the consuming countries. An alternative suggestion, based on laboratory tests showing that solid sulphur has superior resistance to compression and tensile stresses than concrete is that ships made from sulphur should be cast hollow and their holds used to load full cargoes of phosphate or fertilizers.

No doubt it would be possible to mould shipforms from liquid sulphur, but before they could be moved across the oceans, Lloyds Register and the authorities responsible for safety at sea, may have some observations. A claim that they could be drawn behind "little tugs" is subject to doubt as none but the large and highly expensive—to—hire ocean salvage and similar tugs could meet the conditions often experienced in the North Atlantic. A final claim, likely to bring a wry smile to all who have experience of ports and negotiations with dock labour, reads:—

"At destination, all that would be needed is a space cleared on to which the 'ship' could be beached or drawn up. After that it would be broken into pieces as and when required."

The following freight statistics are based on known charterings, save where recent reports are lacking. In such cases 'national' figures, calculated on freights paid for other commodities moving in the same direction, are inserted.

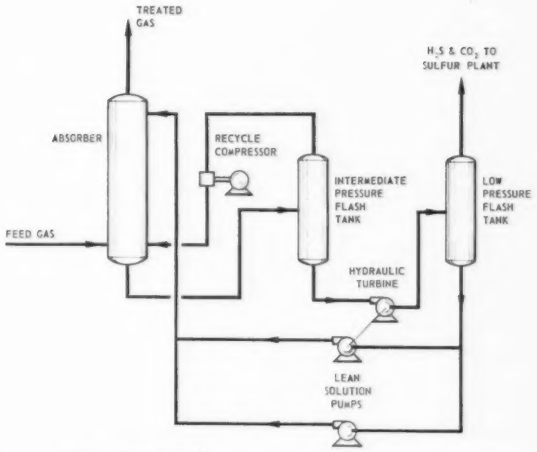
EXPORTING AREA	DESTINATION	FREIGHTS PER LONG TON (Month of August)		
		1961	1960	1959
U.S. Gulf/Mexico	United Kingdom[1]	51s. 0d.	47s. 6d.	42s. 9d.
,, ,, ,,	N.W. Europe[2]	$5.15	$4.90	$4.50
,, ,, ,,	India[3]	$10.05	$9.50	$9.00
,, ,, ,,	Australasia[3]	$12.25	$9.80	$9.73
,, ,, ,,	Brazil[4]	$7.25	$5.40	$4.75
Bayonne	N.W. Europe[4]	19s. 6d.	18s. 6d.	17s. 0d.
,,	United Kingdom[1]	32s. 0d.	32s. 6d.	24s. 6d.
Huelva	Antwerp[5]	20s. 6d.	23s. 0d.	22s. 6d.
Cyprus	Rotterdam[5]	27s. 6d.	25s. 0d.	24s. 6d.
,,	United Kingdom[6]	40s. 0d.	37s. 0d.	37s. 6d.

KEY TO CHARTERING CONDITIONS:—

1 Cargo f.o.b. — ship to pay current cost for discharging.
2 Shipowner to pay 50 cents ton for loading and 40 cents (U.S.) per ton for discharging.
3 Ship pays 50 cents/ton for loading and current rate for discharging cargo.
4 Cargo f.i.o. (no charge to ship for loading or discharging).
5 Ship pays 2s. 6d. ton for loading and 2s. 6d. ton discharge.
6 Ship pays loading cost 2s. 6d. ton and for discharging at rate current in unloading port.

*Sulphur No. 34, June 1960, Page 25

Fluor Solvent H_2S/CO_2 Process for Wintershall A G.



Flow diagram of the Fluor solvent acid gas removal process

LATEST of the several gas purification processes developed by Fluor Corporation Ltd. of California — the Fluor-Solvent Process — is to be used for bulk removal of hydrogen sulphide by Wintershall AG., of West Germany. In addition to removing H_2S, from refinery gases the $2 million installation, which will be located at a recently developed natural gas field, near Dueste, some 30 miles south-west of Bremen, will also remove simultaneously carbon dioxide. To recover the sulphur a Fluor-modified Claus plant will be incorporated.

First in Europe

The Wintershall project marks the first application of Fluor's solvent treating process outside the U.S.A. The newly-developed process is now in commercial operation at the plant of El Paso Natural Gas Company at Terrell, West Texas, where it is being used to clean natural gas containing 53% CO_2 but no H_2S.

Process design for the German unit is being supplied by Fluor, and the company's Dutch subsidiary, Fluor-Schuytvlot N.V. will undertake the engineering materials procurement and construction services. Erection of the Wintershall plant is due to start later this year and to be completed by the autumn of 1962. It will have a design capacity of 28 million standard cubic feet per day of gas containing up to 15% H_2S and 20% CO_2. The purity of the treated gas will meet West German municipal specifications.

New Approach

Fluor's solvent process represents a new approach to the problem of purifying high-pressure gas streams rich in acid gases. It is a simple process and the economics are reported to be quite favourable when compared with other available processes.

Solvents used may be propylene carbonate, glycerol triacetate, butoxy diethylene glycol acetate and methoxy triethylene glycol acetate. All four solvents have the properties needed to ensure that removal of large amount of CO_2 and H_2S from natural gas is economic, thus:—

(a) High solubility capacity for acid gas permits the solvent circulation rate and pumping requirements to be kept to a minimum.

(b) Low vapour pressure at operating temperature eliminates the need for refrigeration, solvent vapour recovery and hydrocarbon recovery systems.

(c) Low hydrogen and hydrocarbon solubility minimizes loss of valuable hydrocarbons or obviates the expense of plant modification to minimize it.

(d) Low viscosity, especially at the lower temperatures at which solvents' CO_2/H_2S solubility is high and vapour pressure low, influences size of equipment, particularly the absorber and mechanical efficiency of pumps.

(e) Low hygroscopicity keeps down the volume of water in the solvent stream thereby limiting reduction of the solvents' capicity for absorbing CO_2/H_2S and decreasing corrosion. The small build-up of water in the feed stream

also obviates the need for feed-dehydrating equipment and process complexity.

(f) Highly stable under operating conditions, non-reactive in the feed, non-corrosive to common metals, the above reagents are readily available at reasonable cost.

Basic Process

Three steps are employed in operating the Fluor solvent process: Natural gas containing CO_2 and H_2S at about 800 p.s.i.g. is fed to the bottom of a conventional absorption column where it contacts, in countercurrent flow, the solvent — propylene carbonate — which is fed to the top of the column at slightly sub-ambient temperature.

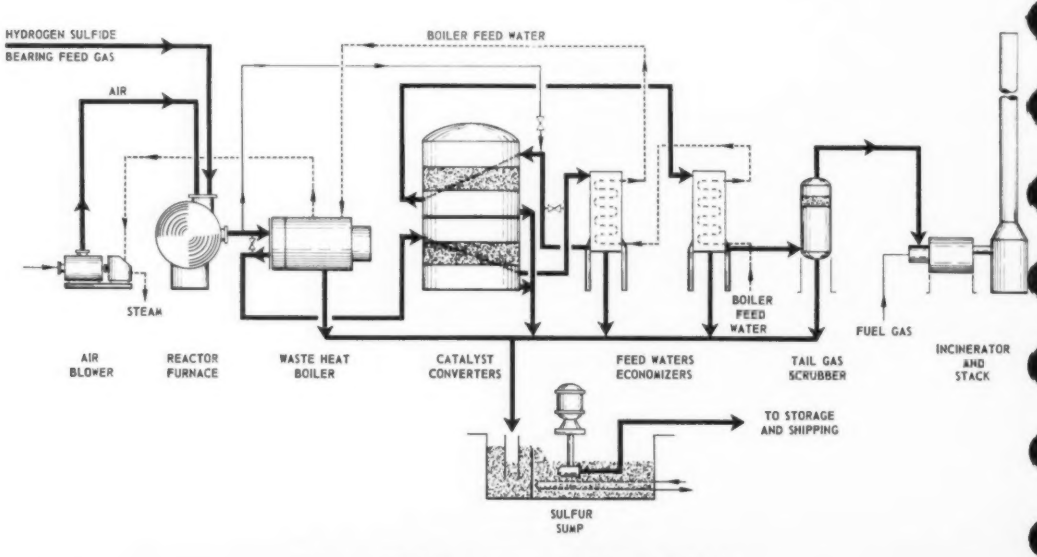
The solvent employed absorbs CO_2, water vapour, H_2S, mercaptans and small amounts of hydrocarbons and then leaves the bottom of the column at a raised temperature because of heat of absorption. The saturated solution then passes to an intermediate flash drum where light hydrocarbons are flashed off and returned as recycle to the raw gas absorber. In the last step the semi-stripped solvent still at a relatively high pressure passes through a power recovery hydraulic turbine and is fed to an atmospheric pressure flash vessel. In this a considerable amount of CO_2 in the solvent is desorbed and in being vented serves to strip water, H_2S and mercaptans from the solvent. Cooled, stripped solvent is then recycled to the top of the absorber.

Fluor Modified Claus Sulphur Process

From the Fluor solvent process treating unit, the acid feed gas passes to the Fluor-modified Claus sulphur plant. Any entrained liquids are removed from the gas by passing it through a "knockout" drum. The feed gas is then burned with a controlled amount of air supplied by air blowers, at about 5 p.s.i.g. Part of the air blower capacity is electrically driven to facilitate start-up operations, while the main blower is driven by a turbine utilizing 250 p.s.i.g. steam.

In the acid gas combustion chamber, part of the H_2S is converted into SO_2 while the hydrocarbons present are burned to CO_2 and H_2O. In addition, a small amount of carbonyl sulphide, COS, is formed by the reaction between H_2S and CO_2. The amount of air is controlled to maintain an H_2S/SO_2 ratio of 2:1 at the outlet of the combustion chamber.

$$2H_2S + 3O_2 = 2SO_2 + 2H_2O$$
$$CH_4 + 2O_2 = CO_2 + H_2O$$
$$H_2S + CO_2 = COS + H_2O$$



Fluor-modified Claus process for Wintershall AG.

Economic Comparison of Treating Processes

	Fluor Solvent	Giammarco-Vetrocoke (air-stripped)	Hot Potassium Carbonate	Water Wash
Plant Investment*	$2,400,000	$3,900,000	$4,600,000	$4,800,000
Direct operating costs				
Fuel gas	130,000	90,000	590,000	206,000
Process water	1,000	5,000	2,000	1,000
Chemical losses	18,000	10,000	6,000	1,000
Operating labour	96,000	96,000	96,000	96,000
Maintenance	104,000	156,000	172,000	192,000
Plant general	62,000	74,000	78,000	83,000
Total direct cost	**411,000**	**431,000**	**944,000**	**579,000**
Indirect operating costs				
Depreciation	240,000	390,000	460,000	480,000
Taxes and insurance	60,000	98,000	115,000	120,000
Interest	72,000	117,000	138,000	144,000
Total indirect costs ...	**372,000**	**605,000**	**713,000**	**744,000**
Total operating costs ...	**783,000**	**1,036,000**	**1,657,000**	**1,323,000**
Treating costs $ MCSF feed ...	$0.020	$0.027	$0.043	$0.034

* Includes royalty and initial chemical charge

Most of the hot combustion gases pass from the combustion chamber to a waste heat boiler in which 270 p.s.i.g. steam is generated and the remainder is by-passed around the waste heat boiler. The cooled gases then flow to a sulphur converter, where sulphur is formed in the presence of a bauxite catalyst.

$$2H_2S + SO_2 = 3S + 2H_2O$$

This reaction is exothermic and results in a converter effluent temperature higher than the inlet temperature.

Gases from the first converter are cooled, and sulphur is condensed in the first economizer. This stream is then mixed with the hot by-pass gases to prevent condensation of liquid sulphur in the second converter bed.

Use of Waste Heat Boiler

Further conversion of H_2S and SO_2 to elemental sulphur is then obtained in this second converter. The gases from the second converter are cooled, and additional sulphur is condensed in the second economizer. Cooling in the economizers is accomplished by heating of boiler feed water. Water is circulated through the second economizer, then through the first economizer and thence to the waste heat boiler.

Cooled gases from the second economizer pass through a tail gas scrubber for removal of any entrained sulphur. The tail gases then flow to the incinerator, where any unreacted H_2S and other sulphur components are burnt to SO_2. Treated fuel gas and flash gas from a rich amine flash drum are used to fire the incinerator which is provided with a 300 feet high stack for dispersal of the combustion products.

Condensed sulphur from the waste heat boiler, converter, economizers and the tail gas scrubber is collected in a sulphur sump. Facilities are being provided at Wintershall for the handling and storage of both solid and liquid sulphur.

Basis for Estimating Plant Operating Costs

Direct Costs	
Fuel gas	$0.16/mm Btu
Process water	$0.10/m Gal.
Chemical losses	Current Prices 1960
Operating labour	Operators $2.75/hr. Foremen $3.50/hr. plus 22% burden to cover insurance vacation and other benefits.
Maintenance	Annually 4% of plant investment, typically 60% labour and 40% materials.
Plant general	Annually 40% total direct labour costs, includes non-operating services and personnel up to and including plant manager.
Indirect Costs	
Depreciation	Annually 10% of plant cost
Taxes and insurance	Annually 2.5% of plant cost
Interest	Annually 3% of plant cost

Low Cost of Plant

Waste gas or gas with a high percentage of components heavier than propane is likely to show losses. An economic comparison of the Fluor solvent process with the hot potassium carbonate, Giammarco-Vetrocoke, and water-wash process is as shown on Page 33.

The German plant, with spare capacity, will cost $2 million to treat 28 million cu. ft./day of raw gas. If $1 million is allowed for the sulphur recovery plant, the cost of the treating unit is $1 million, or 3.6 cents/daily cu. ft. The plant handling H_2S might be pro-rated on the basis of investment. The pro-ratio suggests a cost of about 2.6 cents/1,000 cu. ft. for treating raw gas with 15% H_2S and 20% CO_2.

Berk Commissions New H_2SO_4 Plant

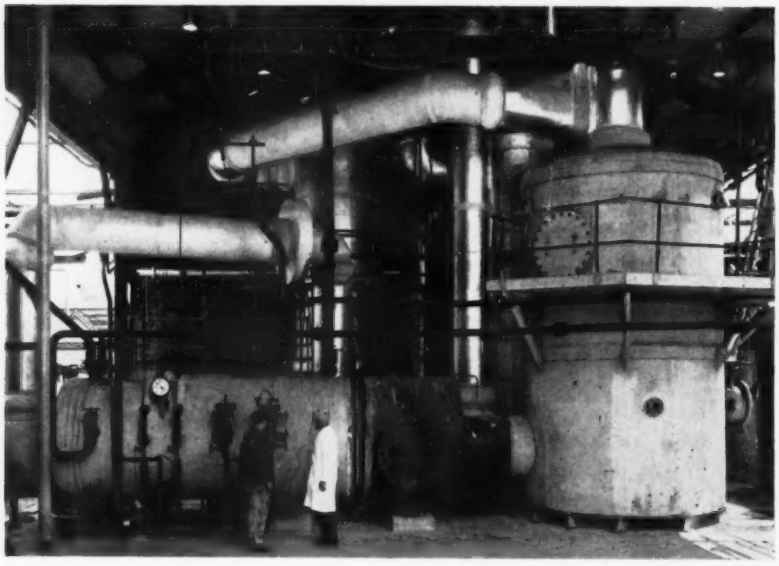
IN MAY a new contact sulphuric acid plant was commissioned by F. W. Berk and Company at the company's Stratford, London, works. The design of the plant was carried out jointly by the company's own staff and Simon-Carves Ltd. The new plant replaces a 24-ton-a-day unit installed in 1939. The company also has a 36-ton-a-day Leonard-type contact sulphuric acid plant which was also built by Simon-Carves Ltd.

The decision to install a new sulphuric acid unit was taken when it was found that technical improvements to increase plant capacity and efficiency of the 24-ton-a-day plant, which had already been incorporated in Berk's second sulphuric acid plant at Stratford, could not be carried out economically in the older plant.

As much of the original plant was still in excellent order, however, and was capable of working at a higher production rate the company sanctioned a scheme for incorporating these units in a new plant layout in which the burner, a four-stage converter, a waste heat and the gas cooling equipment, were new units. The new plant layout is compact, and the plant is in the open air releasing the original plant building for other uses.

Work was started in September 1960 and the plant was commissioned last May.

The waste-heat boiler is of modern fine-tube design giving approximately 1¼ tons of steam per ton of acid produced, and with the amount of catalyst 10% in excess of the minimum requirement, operation has been within the limits recommended by the Alkali Inspectors for a four-stage conversion unit. An air pre-heat stage is included before the burner, there is a quench air addition and an economizer for fuel cooling.



The new contact sulpuric acid plant of F. W. Berk and Company at Stratford

Dimethyl Disulphide for Solvent Extraction of Sulphur

Crystalline sulphur from dimethyl disulphide process

ALTHOUGH large quantities of native sulphur are present in surface deposits, its extraction in elemental form is not economic. The Frasch process is not suitable and melting and autoclaving processes have proved uncompetitive with other sources of sulphur supply, except when in small geographically favoured markets or when encouraged by governments for fiscal reasons. Surface-type deposits are located in Sicily, South America and Japan. Reserves are estimated to be of the order of 200 million tons.

Solvent extraction of sulphur from native ores using carbon disulphide and also perchloroethylene, both effective solvents of sulphur, has been practised in an endeavour to improve the economics of production of sulphur, and disadvantages in using carbon disulphide such as high flammability, high vapour pressure, and toxicity, have marred these attempts. So far, the various companies with experience in this field have only been able to use CS_2 in batch processes.

Solubility of Sulphur in DMDS

Dimethyl disulphide, produced readily from dimethyl sulphide* possesses in theory certain very definite advantages over carbon disulphide. To investigate its possibilities, therefore, Crown Zellerbach Corporation of Camas, Washington, U.S.A., sponsored a research programme at the Colorado School of Mines Research Foundation, involving an investigation of the solubility of sulphur in pure dimethyl disulphide and in components systems, which include dimethyl disulphide as one of the components; an investigation of leaching techniques; design of plant and equipment; and an evaluation of steam stripping and benzene washing for removal and recovery of dimethyl disulphide from barren tailing and crystallized sulphur product.

Finally, a preliminary investigation was made of the market acceptance of a crystallized sulphur product.

Advantages over CS_2

The results showed that: As an extractant of elemental sulphur, dimethyl disulphide has the following technical advantages over carbon disulphide:—

- Adaptability to a continuous rather than batch type of process
- Large solubility change with temperature, permitting crystallization under controlled conditions
- Higher solvent capacity at atmospheric pressure
- Lower heat requirements
- Much less explosion hazard

And the following technical disadvantages:—

- Higher reagent costs
- Formation of small amounts of dimethyl trisulphide during extraction

The unpleasant odour arising from the presence of dimethyl trisulphide appears to be controllable by the addition of organic acids such as benzoic acid to the dimethyl disulphide extraction system.

The method failed to purify a sample of dark sulphur from the Gulf Sulphur Corporation. The impurity was soluble in dimethyl disulphide and recrystallization did not greatly improve the appearance.

The economics of the method were not finally determined by the research programme and a pilot operation would be necessary to

* Sulphur No. 33, April 1961, page 39.

define them accurately. It is suggested however, that dimethyl disulphide at 20 cents a pound would be competitive with carbon disulphide at four cents a pound, and production on a sufficiently large scale could readily reduce the price of DMDS to this level and possibly below it.

Experimental Work

Solubility. The solubility of sulphur in dimethyl disulphide at elevated temperatures is so high that the full capacity of the solvent cannot be utilised in the extraction medium grade ores (20 to 30% sulphur) because more solvent is required to maintain the fluidity of the gangue than to dissolve the sulphur.

It appears from this that it would be possible to reduce solvent costs by diluting the dimethyl disulphide with an inexpensive reagent, at the same time maintaining the same dimethyl disulphide to sulphur ratio as with the pure solvent.

Numerous dimethyl disulphide—inert reagent systems were tried, but it was found in each case that the presence of an inert reagent greatly decreased the solvent power of the dimethyl disulphide. Only two systems seem feasible, the 3:1 and 2:1 dimethyl disulphide — benzene systems, but because of the low boiling point of the 2:1 system, only the 3:1 would be practical.

Solvent Losses

Some cyclic tests were run using this system, but solvent losses were high. In all other respects the system behaved the same as straight dimethyl disulphide.

Leaching. Agitated slurry leaching was investigated using Sicilian sulphur ore containing 26% free sulphur which was stage crushed to a specified size. The samples were then mixed with one half their weight of dimethyl disulphide or the 3:1 system and the mixture heated to 85 to 95°C and filtered. The gangue was washed with a small amount of dimethyl disulphide and several small portions of benzene, and was then dried and analysed.

It appears that the ore should be ground to a least −10 mesh to achieve maximum leaching efficiency, that the required contact time is quite short and that both solvent systems are equally effective.

Mesh size	Solvent	% sulphur in gangue	% extraction
−¼in.	Dimethyl disulphide	2.34	91.3
−¼in.	Dimethyl disulphide-benzene	2.35	91.2
−10 mesh	Dimethyl disulphide	0.27	99.2
−10 mesh	Dimethyl disulphide-benzene	0.23	99.3

Percolation leaching, in which the hot solvent was passed upwards through a tall bed of ore, was also investigated in an attempt to obviate the possibly expensive liquid-solids seperation in the agitated slurry leaching method. Results indicated that the sulphur-containing dimethyl disulphide was not readily displaced from the ore voids by fresh solvent and the method would very likely be inefficient. The principle of an ore bed moving downward through a tall column might, however, be a convenient way of steam stripping the dimethyl disulphide from the gangue and crystallized product.

An attempt was also made to suspend the ore in water while dimethyl disulphide was used as a separate phase to dissolve the sulphur. Unfortunately, although the sulphur was dissolved, the solvent-sulphur phase became dispersed as small droplets in the water-gangue mixture. Because of this and the danger of corrosion in the system, the method was not investigated further.

Crystal Growth. Large crystals can be formed relatively easily, provided that the cooling rate is carefully controlled. The crystals produced are uniform octahedra which are quite hard.

Cyclic Leaching - Crystallizing Tests. To achieve a continuous process requires leaching the sulphur from the ore to produce a saturated solution, followed by separation of the gangue from the saturated solutions, crystallization of the sulphur product, and recycling of the mother liquor. Any filtration of the hot saturated liquor must be done under pressure.

Equipment was constructed which would allow agitated leaching followed by pressure filtration and crystallization, all in a closed system. High amounts of sulphur were found in the tailings and were attributed to the inadequate washing inherent in the operations of the

extractors. Solvent balances were rather low but this is attributed to vapour losses through the reflex condensers and handling losses in manipulation of the small equipment. Solvent recovery is expected to be greater than 95% in a large plant.

Two Methods Investigated

There was a build-up of dimethyl trisulphide during the recycle tests and two methods were investigated for eliminating this. In the first, crystallized mother liquor was passed through a column of absorbent material such as activated charcoal or silica gel. It was found that charcoal still left an appreciable trisulphide odour, while with silica gel sulphur deposited out, blocking the column. This occurred even with solutions which were definitely not supersaturated.

The second method involved using a weak organic acid to prevent the formation of trisulphide. According to literature reports, the reaction between dimethyl disulphide and sulphur to form the trisulphide is base catalysed. The Sicilian ore used contained considerable quanties of calcium carbonate.

Retarding Trisulphide Formation

Phenol, *p*-nitrophenol, benzoic acid and glacial acetic acid were added in small quantities to the solvent. It was found that, with the exception of glacial acetic acid, all the acids were effective in retarding trisulphide formation, benzoic acid being by far the most effective. Some co-precipitation or occlusion of *p*-nitrophenol occurred.

Steam Stripping and Benzene Washing. The efficiency of steam stripping to remove and recover dimethyl disulphide from the wet gangue and crystallized sulphur was checked by boiling the equal volumes of water until about half the water was distilled off. With the gangue samples this was done at 95°C, while with the sulphur samples the distillation was done under slight vacuum at 70 to 80°C to minimize formation of trisulphide.

Typical recoveries from gangue were 85 and 96% and from sulphur 86 and 64% dimethyl disulphide. This low recovery was attributed partly to formation of an emulsion in the liquid which did not separate readily. There was no odour of dimethyl disulphide after stripping, although the sulphur samples had a faint odour of dimethyl trisulphide. A considerable amount of trisulphide odour was present in the distillate, indicating that it too could be steam stripped.

Samples of gangue and crystallized sulphur were washed with benzene and dried at low temperatures. In all cases benzene seemed to be effective in removing dimethyl disulphide but not the trisulphide.

Little Solvent Occluded

Tests showed that the carbon content of samples of crystallized sulphur product which had been steam stripped and washed with benzene was negligible, indicating that very little solvent is occluded with the sulphur crystals.

Other Sulphur-Bearing Materials. An ore containing 45% free sulphur, from Zahn and Co., Germany, was stage crushed to – 10 mesh and extracted with dimethyl disulphide continuing 2% benzoic acid. An extraction of 99.7% was obtained, the product being 99.97% pure. From a Philippine ore containing 31% sulphur, a 98.5% extraction of 99.9% sulphur was obtained.

A sample of flotation concentrate produced from the Sicilian ore, containing 85% sulphur, was extracted with dimethyl disulphide. The sulphur was upgraded to 99.94%, but after three extraction cycles there was a definite odour of dimethyl trisulphide. However, because of the low cost ($5 to $6 a ton) of the flotation process, it might be economically possible to combine it with the extraction process, since gangue processing would be greatly reduced and the full solvent capacity could be utilised.

Corrosion. Investigations indicate that if mild steel is used, only very small amounts of water can be tolerated in the system. In cyclic tests it was shown that the hot solution dissolved tygon and neoprene rapidly, and was very corrosive on copper and brass.

Cost Comparisons

In carbon disulphide extraction plants the sulphur is recovered from the carbon disulphide by distilling away the solvent and melting the sulphur. Zahn and Co. reports

that this requires 3,500lb. of steam per ton of sulphur. The dimethyl disulphide process on the other hand only requires sufficient heat to raise the temperature of the dimethyl disulphide solution from 60 to 85°C together with the heat of solution of the sulphur and the small amount of steam necessary to remove residual dimethyl disulphide from the sulphur crystals. The total amount would be much less than for carbon disulphide process.

Since the amount of dimethyl disulphide required per ton of sulphur is only one fifth the amount of carbon disulphide, and assuming a price of 4 cents per lb. for carbon disulphide and 20 cents per lb for dimethyl disulphide, the total solvent costs for the two processes would be equal.

Solvent Loss

Zahn and Co. suggests a solvent loss of 1 to 2% of the total for carbon disulphide extraction plants. The Colarado School of Mines Report suggests that it is conservative to assume a solvent loss of 2% of total solvent used, especially in view of the high vapour pressure of carbon disulphide.

The explosion hazard of dimethyl disulphide is very small compared with carbon disulphide and no special precautions are necessary in its use. The toxicity hazard is also expected to be less than with carbon disulphide.

The product from the dimethyl disulphide process is crystalline, but the report suggests that this might be preferable for some applications. In addition, the crystals could be crushed to fine powder or melted if necessary.

The extraction efficiency would be at least as good as with carbon disulphide and laboratory tests suggest that it might be even better.

Continuous Process

It is suggested that the process could easily be made continuous resulting in saving of labour, solvent, and make-up costs. In theory the carbon disulphide process is of course also capable of being worked continuously by substitution of an evaporator for a crystallizer, but companies with experience in the carbon disulphide process state that it must be operated batchwise.

A possible flow diagram for a continuous process using dimethyl disulphide is shown.

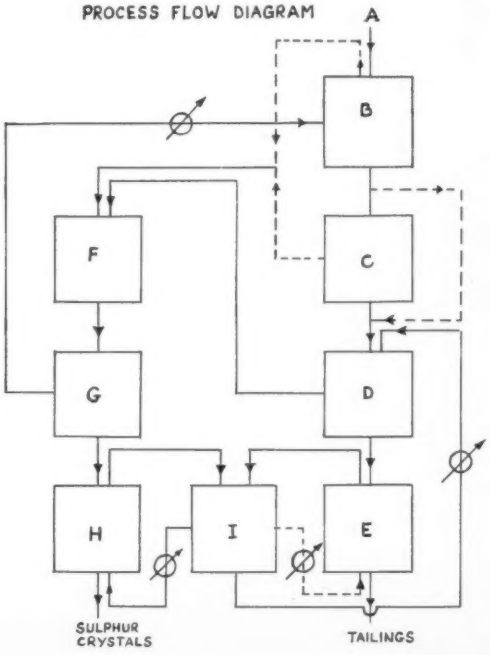


Diagram of continuous extraction process using dimethyl disulphide:—

A. −10 mesh sulphur ore preheated to 85°C.

B. Extractor. This could be either: A column into which the ore is fed at the top and removed at the bottom and the dimethyl disulphide mother liquor from the crystallizer preheated to 85°C is pumped in at the bottom, taken off at the top, and the sulphur-pregnant solution clarified by solution; or it could be an agitated vessel into which ore and dimethyl disulphide-sulphur mother liquor are fed continuously and a hot slurry discharged continuously after adequate retention time.

C. If a column extractor were used, **C** would be bypassed. If an agitated vessel were used, **C** would represent a continuous centrifugal filter or other device for making a hot liquids-solids separation of the gangue from the hot sulphur-pregnant dimethyl disulphide.

D. A device for washing the gangue with hot dimethyl disulphide from **I.**

E. Removal of residual dimethyl disulphide from the gangue, either by steam stripping or by heating in a rotary kiln.

F. One of the various types of evaporative-cooling or cooling crystallizers, where the sulphur would be crystallized and a slurry of sulphur crystals and mother liquor would be fed to

G. Where sulphur is separated and washed with fresh dimethyl disulphide.

H. Steam stripping to remove residual dimethyl disulphide from the sulphur crystals.

I. Condenser for steam and dimethyl disulphide from **E** and **H.**

current events

CANADA

BA Sulphur Recovery Plant

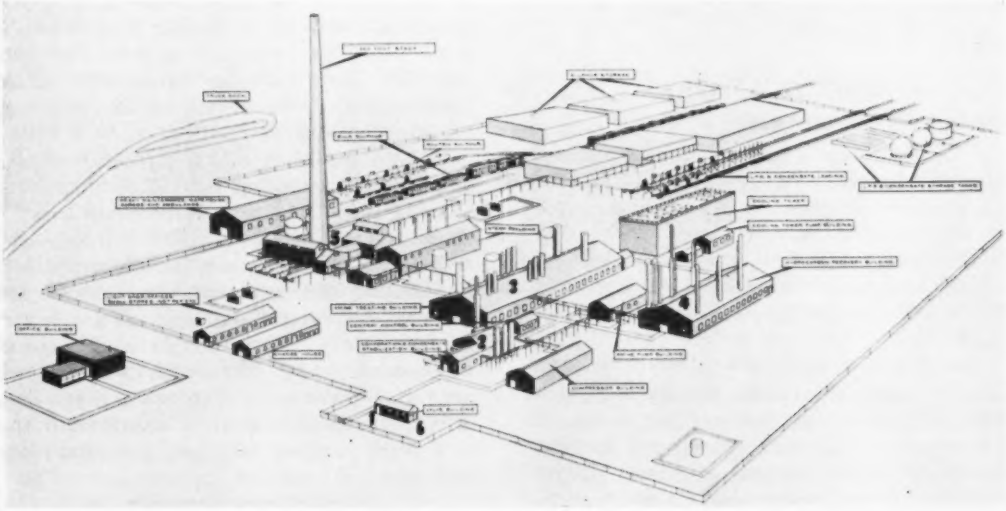
Two sulphur producing plants, both in Alberta, Canada, are at present being operated by The British American Sulphur Company: at Pincher Creek, with capacity of 675 tons a day, and at Nevis, with capacity of 70 long tons a day. A third plant is now being built at Rimbey, also in Alberta, with a planned capacity of 233 long tons a day. The process design, procurement and construction for the sulphur recovery facilities at the Pincher Creek plant were provided by Ralph M. Parsons Company. Expansion at this plant has proceeded in three stages and hydrogen sulphide which makes up almost 11% of the gas stream of 180 million s.c.f.d. is processed in three sulphur recovery units, each of 225 long tons capacity of S per day.

All three sites are connected to the railway, and sulphur is delivered from them in specially-designed insulated railway tankers. The tankers are supplied by British American at no cost to the customer. Capacity of each tank car is 62.5 long tons.

In the company's view the economic production of sulphur from sour natural gas depends to a great degree on the suitability and availability of transport for the purified sulphur and to compete with sulphur from other sources, sulphur from natural gas has to be moved simply and cheaply from the refinery.

Sulphur Production at Carstairs

Expanding its present 70 million cubic feet per-day gas processing plant near Carstairs, Alberta, to treat 200 million cubic feet a day is Carstairs Operators' Committee comprising Gas Transmission Company, Shell Oil of Canada Limited, Canadian Superior Oil of California Limited, Pan American Petroleum Corporation, Alimex Limited and 21 other companies. The plant is being enlarged to enable sour natural gas from deposits at Carstairs and Crosfields to be processed. A product recovery unit will remove daily about 7,000



British American Oil Company's Pincher Creek gas processing and sulphur plant. Numbered points below refer to numbered buildings in drawing where processing steps occur.

1. Raw gas enters the plant from field. 2. Condensate separated and stabilized. Process gas dehydrated before amine treating. 3. Hydrogen sulphide is removed by amine treating. Process gas is now sweet. Process gas proceeds to (4). Hydrogen sulphide proceeds to (5). 4. LPG (propane and butane) and additional condensate recovered. Process gas is now dry. 5. Hydrogen sulphide is converted to elemental sulphur. 6. The sweet dry residue gas is delivered to Alberta Gas Trunk Line.

barrels of liquid hydrocarbons from the gas stream and sulphur will be recovered. The gas will be sold to Trans-Canada Pipe Lines Limited and to Alberta and Southern Gas Company Limited.

An amine desulphurization unit will be incorporated in the Carstairs plant to remove hydrogen sulphide from the gas feedstock. The H_2S will be fed from the regeneration still of the amine unit to a modified Claus sulphur processing unit, which is to have a daily capacity of 40 s. tons of brimstone.

Carstairs Operators' Committee has awarded a $3 million contract to Fluor Corporation of Canada Limited to engineer, procure materials for, and construct the new extension. Construction began in May and when completed in November this year the plant will be operated by Home Oil Company Limited.

At the present time in Canada there are several other large sulphur recovery plants under construction. Of these two are being constructed for Jefferson Lake Sulphur Company by Ralph M. Parsons Company at East Calgary and Coleman, Alberta*, with daily capacities of 863 long tons and 400 long tons brimstone respectively, and one for Shell Oil of Canada at Pincher Creek, with a daily capacity of 1,400 long tons of brimstone.

UNITED STATES

Stauffer's New Route to SO_2

To make liquid sulphur dioxide, sulphur is usually burned with air when a 14 to 15% SO_2 stream is formed. The SO_2 is concentrated by absorption in solvents such as water or dimethylamine and then stripped out, dried, cooled, compressed and liquified to yield a production containing less than 50 p.p.m. water.

At the new liquid SO_2 plant of Stauffer Chemical Company at Baton Rouge, La., which came on stream earlier this year, use is made of a new process for which patents are pending. Details are being withheld at present, but it is known that Stauffer reacts sulphur with sulphur trioxide.

$$S+2SO_3=3SO_2$$

Although not a new reaction the problem has difficulties in control. Stauffer Chemical, however, considers that this route simplifies the gas purification problem since the end reaction product is essentially 100% SO_2. Also, the company has available pure SO_3 from its oleum plant on the same site.

It is believed that in the new process, molten sulphur enters a tile-lined reactor containing a 30% SO_3 oleum solution. At 230°-250°F SO_2 gas is produced which is passed through a sulphur filter, an H_2SO_4 drying tower and a demister, followed by a conventional liquefaction procedure.

Uranium Processing by Petrotomics

Petrotomics Company Inc. now has under construction at Shirley Basin, Wyoming, U.S.A., a uranium processing plant which will use a new process. Rated capacity of the plant will be 500 s. tons a day. It will be a conventional acid leach plant using solvent extraction. Ore will be crushed through a 30in. by 40in. jaw crusher designed to handle large pieces of cemented material which represents about 10% of the ore, the remainder being partially cemented sand. Secondary crushing will be carried out in a small impact crusher and grinding in a 6in. by 8in. ball mill in a closed circuit, with cyclones. Leaching will be effected in five 14ft. by 14ft. wood stave leach tanks, using an estimated 80lb. per ton sulphuric acid plus 2lb. per ton sodium chlorate ($NaClO_3$). Sulphuric acid consumption is expected to be in the region of 20 short tons per calendar day.

From the leach tanks, separation of the liquid will be made in six C.C.D. thickeners, 55ft. by 12ft. Thickener overflow will pass for clarification through a 22ft. by 12ft. clari-flocculator, through a pre-coat filter, and into a standard solvent extraction unit, using kerosene as a solvent and amine as a collector. Precipitation will be accomplished by use of magnesium oxide. The precipitate obtained will be washed in a filter press, dried in a skinner roaster, crushed to specification size in a small hammer mill, and packaged automatically.

As yet Petrotomics Company is undecided whether or not to make its own sulphuric acid. Economic production would, in view of the relatively small requirement of sulphuric acid to be consumed, necessitate outside

* Sulphur No. 33, April 1961, page 35.

disposal of at least 20 s. tons per day of acid in a market now supplied by established manufacturers. By virtue of the remote location of the plant, however, it may prove to be economic for the company to establish a small capacity sulphuric acid plant in conjunction with a milling plant. A decision is expected to be made in August.

Virginia-Carolina Interest in Texas International Sulphur

Virginia-Carolina Chemical Corporation has acquired one million shares of stock in Texas International Sulphur Company, Houston, Texas, thereby receiving a 20% interest.

As part of the purchase agreement, Virginia-Carolina has signed a 10-year contract to buy large quantities of sulphur from Central Minera S.A., Texas International's operating subsidiary in Mexico, and to provide technical and management assistance to Texas International during the tenure of the contract.

Three Virginia-Carolina executives have joined in Texas International board; they are Edward R. Adams, vice-president of finance, Douglas W. Laird, vice-president of purchasing and R. David Smith, general counsel.

Central Minera S.A. produced at its Texistipec dome 4,800 tons Frasch sulphur in June, compared with 2,800 tons in May and similar quantities in the preceeding months. Output is to be raised progressively before the end of this year.

Virginia-Carolina mines and processes phosphate rock, and it has more than 20 sulphuric acid fertilizer plants located in Alabama, Georgia, Florida, Virginia and North and South Carolina, Louisiana, Ohio and Tennessee. The company has under construction at Nicholas, Florida, a 300,000 tons a year triple superphosphate plant and a 100,000 tons a year ammonium phosphate plant under construction which are due to be completed by December 1961.

Consumption of sulphur by Virginia-Carolina is estimated at 180,000 s. tons a year, but the increased production of triple superphosphate and the new ammonium phosphate plant are likely to raise consumption by 60% to 70%.

NORWAY

Sulphuric Acid Production to Increase

Sole producer of zinc in Norway, Det Norske Zinkkompani A/S, is planning to raise annual production capacity at its plant in Odda, Western Norway, by 17,000 tonnes annually to 65,000 tonnes metal. Capacity for sulphuric acid is to be increased by 50,000 tonnes to 100,000 tonnes (100% H_2SO_4). Phosphoric acid capacity is also to be increased. The expansion scheme will be completed in 1965-66 at an estimated cost of Kr. 40 million (£2 million).

Det Norsk Zinkkompani, which is a subsidiary of the Belgian Cie. Royale Asturienne des Mines, has a smelter and sulphuric acid plant at Eitrheim, near Odda. The sulphuric acid plant is a Petersen tower type with a daily capacity of 150 tonnes (100% H_2SO_4). Acid output is consumed captively in the company's zinc and superphosphates plants.

The increase in sulphuric acid production is to be effected by utilizing fully the present and additional sulphurous smelter gases arising from the increased zinc smelter production and it is expected that it will be employed in the planned expansion of the company's phosphoric acid capacity. Superphosphate production at Det Norsk Zinkkompanie amounted to some 85,000 tonnes in 1960, composed of grades containing 18.5%, 30% and 45% P_2O_5 and binary grades containing 17.5% and 23.5% P_2O_5.

ITALY

Sulphur Refining Plant at Licata

Ente Zolfi Italiani recently concluded an agreement with Snia Viscosa of Milan for the installation at Licata of a small refining plant to treat sulphur concentrates and produce refined sulphur.

The new plant is being built by Snia Viscosa and will be managed by EZI. Expected to be in operation by the end of the year, it will have a daily capacity of 200 tonnes of sulphur concentrates containing 90% S in the dry state and 15% moisture. Output will be about 140 tonnes a day of high purity (minimum 99.5% S) molten sulphur, all of which will be taken up by Snia Viscosa.

FRANCE

Cie St. Gobain's New Acid Plant

At the L'Oseraie works near Avignon of Cie St. Gobain the principal products made are sulphuric acid and fertilizers. With the growing consumption of fertilizers in south-east France promoted by irrigation of the Bas-Rhône and Languedoc areas, sulphuric acid requirements have increased and Cie St. Gobain has installed at L'Oseraie works a new sulphuric acid plant designed by the company and using a St. Gobain catalyst.

A novel feature of the new plant is the recovery of the heat of the sulphur burner and of generation of electricity in a central boiler section from by-product strain. Sulphuric acid production at the new plant is 220 tons a day 100% H_2SO_4 based on recovered sulphur from Lacq.

Originally sulphuric acid was produced at this works from Sicilian sulphur using the lead chamber process developed by Gay-Lussac. In 1857, a decree by Louis Napoleon Bonaparte authorized the use of pyrites which was used here as raw material until recovered sulphur became available.

L'Oseraie works also supplies sulphuric acid to local industries, especially those manufacturing textiles and petrochemicals in the Berre region.

At the present time Cie St. Gobain is engaged in building a similar sulphuric acid plant at Thann for Société des Produits Chimiques de Thann and Mulhouse, the important TiO_2 pigment manufacturer.

YUGOSLAVIA

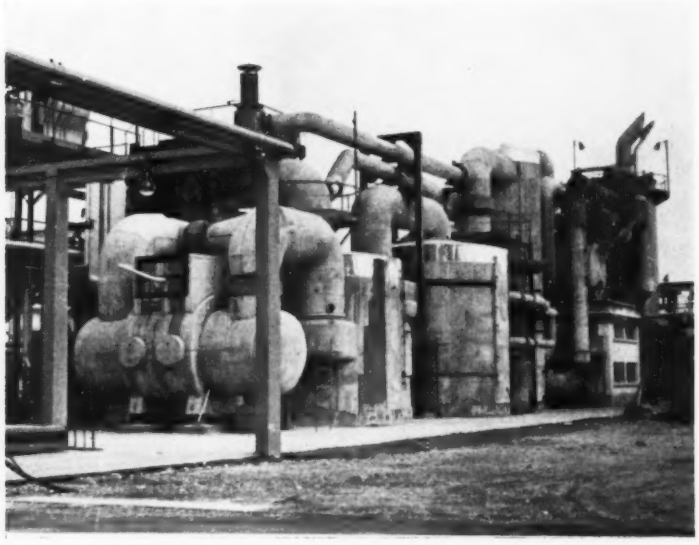
Bor Phosphate and H_2SO_4 Plants

Sulphuric acid production in Yugoslavia in 1960 amounted to 130,000 tonnes 100% H_2SO_4, a modest increase over the previous year's output of 127,720 tonnes.

The Bor Prahovo plant now coming on stream will raise production to 490,000 tonnes by next year. The capacity will be raised by stages, the first to 230,000 tonnes and in the final stages to 570,000 tonnes, when superphosphate production will be one million tons a year. The Prahovo superphosphate works will be the largest in the world.

At Bor, sulphuric acid is produced from the waste gases of copper smelter which handles copper ores from the rich copper mines in Bor and Majdanpek. The new copper works at Bor which has been designed by Enterprise R. and J. Moritz of France, produces almost 50,000 tons of copper annually.

The Bor plant comprises five multi-hearth roasting furnaces supplied by Est. Alfred Maguin and a reverberatory furnace 30 metres long and 10 metres wide which replace water-jacketted furnaces. The new furnaces



The sulphuric acid plant at L'Oseraie plant of St. Gobain

allow the use of other fuels e.g. pulverized coal, and the recovery of waste heat.

The large burners, converters and machinery for casting the anodes have been constructed by Ateliers and Forge de la Loire of France. Sulphurous gases after leaving the furnaces pass through electrostatic dust precipitators, the dust being delivered to a mixing section for disposal, and then proceed to the Peterson sulphuric acid plant. The sulphuric acid plant has a capacity of 1,000 tonnes of 100% H_2SO_4 daily, which is used in production of 50,000 tonnes of calcium superphosphate a year. The sulphuric acid is transported by a new railway line alongside the River Danube which is used to transport North African phosphate rock to the superphosphate works. Equipment at Prahovo includes six Moritz grinding mills and four Moritz continuous superphosphate dens. Automatic handling is used where possible.

At Zorka Sabac, finely ground phosphates for direct spreading on land are prepared. Two Moritz grinding mills handle 10 tons an hour of phosphate raw materials.

In course of erection at Kosovska Mitrovica is a complete works for production of calcium superphosphate. The plant is of identical designs to the Prahovo works, but is only half of the latter's capacity. It, too, is being constructed by Moritz.

U.S.S.R.

Automatic Acidity Control in Ammonium Sulphate Manufacture

At the Enakievo Coke and Chemical Works automatic equipment has been installed at the by-product ammonium sulphate plant to maintain the acidity of the saturator bath, within the range 5 to 7% H_2SO_4.

The acidity of the mother liquor is measured by a floating electrode unit which was developed by TSLA (Central Laboratory of Automation). It consists of a glass electrode and a twin resistance thermometer. Originally the unit was placed in the crystal receiver, but, because of frequent breakages during the periodic agitation of the solution and the effect of resins in the liquor on the electrode, it was transferred to a special flow reservoir. The flow from the crystal receiver enters at the bottom of this reservoir and the outflow passes to the saturator.

The electrical circuit is completed and contact established with the solution by means of a calomel comparison electrode which has a constant e.m.f. This electrode is connected to the solution by means of a contact bridge filled with potassium chloride.

The e.m.f. of the combined calomel glass electrode is proportional to the pH of the solution. By measuring this e.m.f. with a potentiometer graduated in pH units both the acidity of the solution and its free acid content can be determined.

A high-resistance potentiometer (type EPIV-371) is used, having a two-position controller (type DTP-240) with a motor relay and a contact unit which is kinematically linked to the recorder pen through a differential lever mechanism.

When the pH value agrees with the preset value the contact system of the controller unit remains open. When the pH of the system alters, the contact system is displaced, switching on a motor relay which, in turn, operates a magnetic unit which controls the auxiliary electrical mechanism and the associated control valve. By increasing or decreasing the flow of acid from the storage tank in this way the acidity of the solution is maintained.

Control has resulted in the production of better quality material by economic concentration and has reduced decomposition and attendant ammonia losses resulting from weak solutions.

CZECHOSLOVAKIA

Sodium Pyrosulphite from SO_2 in Waste Gases

Sodium pyrosulphite which is used to preserve ensilaged fodder, can be prepared from SO_2 in waste gases, using a process described by R. Klinecek and J. Betthelm.

Sulphur dioxide is absorbed in a circulating solution of sodium carbonate containing some sodium pyrosulphite. Sodium carbonate is added to keep the proportion of acidic and alkaline components (S_2O_5 : NaOH) at about 0.85:1. The precipitated sodium pyrosulphite is removed by a hydrocyclone of suitable dimensions.

JAPAN

Titanium Dioxide Production Difficulties

A strike at Ishihara Sangyo Company, which has lasted over 60 days, is seriously affecting Japan's titanium dioxide production. The product is now in short supply and although other producers are operating plants at full capacity, stocks are now so low that the Japan Paint Export Promotion Association is importing titanium dioxide. At the end of August a shipment of some 1,500 tonnes arrived.

Price of the imported material is higher by 50 to 60% than the domestic price, 50,000 more yen at least and in the case of titanox, 100,000 yen higher, because of the U.S.A. sales tariff. Cost of titanium dioxide from Farbenfabriken Bayer AG. is 20% lower than that of the U.S., and hence the greater part of the Japanese order has gone to Bayer AG.

According to the Japan Inorganic Chemical Industry Association production of titanium dioxide in May was 2,271 tonnes (anatase 2,061 and rutile 210 tonnes) a decrease of about 50% compared with production in April (4,508 tonnes) and March (5,430 tonnes) and nearly 60% compared with August.

Combined productive capacity of the eight plants producing titanium dioxide in Japan totals 5,580 tonnes a month. Ishihara Sangyo Kaisha Limited is the leading producer with a monthly capacity of 3,000 tonnes, and has plans in hand to expand production. The other large producers, each with a monthly capacity of 600 tonnes, are Titanium Industry Company Limited, Teikoku Kako Company and Furukawa Mining Company Limited. The last two companies are planning to increase capacity by 400 tonnes a month by 1967. Sakai Chemical Industry Company Limited, a small producer with a monthly capacity of 230 tonnes, is to expand production by 500 tonnes a month in 1962.

Chugoko Sangyo's New Process for CS_2

A new process for the manufacture of carbon disulphide which uses a fluidization technique and hydrocarbon raw materials, has been developed by Chugoko Sangyo Company.

Advantages claimed for the new process are:—

(1) Changeover to a cheaper coke material from low temperature carbonization of lignite coal.

(2) Thermal efficiency of the furnace employed is twice that of the existing type furnace, with consequence saving in fuel.

(3) Cost of production is reduced by 5,000 to 6,000 yen (£5 to £6) per tonne and is expected to be around 30,000 yen per tonne of carbon disulphide.

Development work, which was begun in 1955, has been assisted by a Government grant from MITI of 2,750,000 yen. A pilot-plant has been in operation at the company's Tsurumi plant.

Insulated capacity in the form of retorts is 1,100 tonnes CS_2 per month, and the output of 900 tonnes a month is being sold to Kurashiki Rayon Company. Construction of a furnace with a monthly capacity of 300 tonnes is nearing completion and operation of the new facility is due to begin by September. The investment cost is estimated at 30 million yen (£30,000).

Japanese Titanium Dioxide Producers

Company	Plant	Capacity (monthly)	Expansion Plans
Fuji Titanium Industry Limited ...	Kobe	350	No expansion planned
	Hiratsuka	180	180 tonnes a month expansion in 1962
Furukawa Mining Company Limited	Osaka	600	400 tonnes a month expansion in 1962
	Yokkaichi	3,000	Plans in hand but not finalised
Mitsui Metal Mining Company Limited	Hibi	20	No expansion planned
Sakai Chemical Industry Company Limited ... ... (Sakai Kagaku Kogyo K.K.)	Osaka	230	500 tonnes a month expansion in 1962
Teikoku Kako Company Limited	Okayama	600	400 tonnes a month expansion in 1962
Titanium Industry Company Limited (Chitan Kogyo Kabushiki Kaisher)	Yamaguchi	600	No expansion planned

Laporte Industries Now Reaping Benefit From Increased Output of Titanium Dioxide

"We are living a world of change . . . But a world of change is also a world of challenge."

P. D. O'Brien Chairman Laporte Industries

GROUP profit for Laporte Industries Limited for the year ended 31 March 1961 of £3,333,525 before taxation is not substantially different from that of the previous year (£3,147,943). The general level of trade has been satisfactory but the company has, in common with many others in the chemical industry, experienced higher costs, increased competition and reduced profit margins.

Over the last 10 years the history of Laporte has been one of growth, and the company's chairman, Mr. P. D. O'Brien, records that between each major advancement there has been a period of consolidation and the company is broadly in that position to-day. It is reaping the benefit of past capital expenditure, but new plants are being erected which are not yet contributing to group earnings.

Laporte Titanium Limited

At Stallingborough, Lincs., a £3 million expansion programme is up to schedule and the company has begun to reap some benefit from the sale of increased output of titanium pigment.

A large and modern sulphuric acid plant to supply the titanium oxide operations has been commissioned and there are now three sulphuric acid plants at Stallingborough which makes the company independent of external sources of supply.

Yorkshire/Derbyshire Companies

Profits from Laporte Acids Limited were reduced owing to lower prices prevailing for sulphuric acid for general sale and increased expenses.

In the previous financial year, Sheffield Chemical Company Limited, James Wilkinson and Son Limited, and Glebe Mines Limited were acquired, the last-named processing native Derbyshire fluorspar, some of which Wilkinson's further convert into fluorine compounds. Laporte is consolidating its interests in fluorspar and has acquired Cupola Mining and Milling Company Limited, owners of mineral deposits and a fluorspar processing plant capable of substantial development, and also Longstone Edge, a rich mineral-bearing area. Sales of fluorspar and fluorine compounds are developing rapidly.

Peter Spence and Sons Limited

Acquired in June 1960, this company's chemical products include notably sulphuric acid, organic titanium compounds, salts of aluminium and a range of catalysts principally based on aluminium.

G. D. Holmes Limited

As Laporte Titanium Limited and Laporte Acids Limited receive a considerable volume of raw materials by barge on the River Humber, shares have been

Rotary calciners in the course of assembly. These are part of the £3 million expansion scheme of Laporte Titanium Limited at Stallingborough, Lincs. The expansions will increase TiO_2 production from 30,000 tons to 50,000 tons by 1962

purchased in G. D. Holmes Limited, which also embraces Goole Docks Fresh Water Boat Company Limited; these companies operate between them some 32 vessels.

Overseas Companies

The Australian subsidiary Laporte Chemicals (Australia) Pty. Limited, Sydney, N.S. Wales, showed a reduced trading profit during the year under review due to the depressed economic conditions which temporarily prevailed in Australia.

Laporte's interests in Canada have been extended by the recent acquisition of Howards and Sons Limited of Ilford. This company has a wholly-owned subsidiary, Howards and Sons (Canada) Limited, with works at Cornwall, Ontario. Plans are in hand to install additional plant for new products.

Research and Development

Mr. O'Brien indicates, in his report, that there is a pressing need to devote attention to longer-range research in broader fields and greater emphasis is being placed on the establishment of a stronger group research team. The total expenditure on research and development represents a significant part of the company's budget.

The Future

Such is the faith of Laporte in the future prospects of titanium dioxide that "certain decisions have been taken which we believe will enhance the opportunity of the company to share in its development overseas."

A £4 million titanium dioxide plant is being established at Bunbury, Western Australia, based on local ore supplies. Australia, remarks Mr. O'Brien, is a large consumer of titanium dioxide, and it is expected that there will be no difficulty in finding a ready market for the output of the plant.

Referring to the agreement with American Potash and Chemical Corp., Mr. O'Brien reports that although titanium oxide is manufactured widely in the U.S. it is not at present made on the West Coast. Design teams on both sides of the Atlantic are now working out plans.

In India Laporte Chemicals Limited has a satisfactory working arrangement with the Bombay Dyeing and Manufacturing Company Limited with regard to hydrogen peroxide and Laporte now proposes to extend its interests in conjunction with the Indian partners by the establishment of a new company which will manufacture titanium oxide under an agreement with Laporte Titanium Limited.

Finance

Total net assets have risen from £18.9 millions at 31 March 1960 to £26.5 millions at the end of March 1961, the latter including the assets of the newly-acquired subsidiary, Howards and Sons Limited.

To bring the group's plans to fruition heavy capital expenditure will be involved, Mr. O'Brien states, and it will therefore be necessary to raise additional finance, in one way or another, in the future—possibly within the next 18 months.

Ketjen Reports Sulphuric Acid Plants Worked at Full Capacity in 1960

DURING 1960 a new sulphuric acid plant based on sulphur as feedstock was installed at Ketjen (Koninklijke Zwaveluurfabrieken voorheen Ketjen) Amsterdam, and is reported to be operating satisfactorily. Construction of a phenol plant was started, together with a factory for phenol derivatives. Capacity of the phenol plant is expected to be 10,000 tons a year, most of which will be used by the company for the manufacture of products such as diphenyl propane (D.P.P.), production capacity of which has been expanded in response to greater demands. The plant will also produce sodium sulphite. The main raw materials will be benzene, sulphuric acid and caustic soda. Ketjen will use its own sulphuric acid; caustic soda will be supplied by Royal Dutch Salt Company and benzene by Dutch State Mines.

Demand for D.P.P. has risen considerably and the plant has been expanded.

Sulphur Dioxide Sales

Ketjen's sulphuric acid plants worked at full capacity throughout the year and sales were good; prices, however, tended to be lower. Sales of sulphur dioxide were high. In 1961 production of calcium permanganate will be discontinued in Holland, and a new company formed, Boots-Ketjen, will have as its main interest the sale of calcium permanganate, production of which is to be started by Boots Pure Drug Company Limited at Nottingham, England.

Merger Plans

Negotiations were started in 1960 between Ketjen and Royal Dutch Salt Company regarding more intensive co-operation between the two.*

Finances

Gross profit in 1960 of Ketjen N.V. and its associated companies was fl.22,776,000, of which Ketjen alone accounted for fl.20,379,250. After deducting depreciations and other charges the profit remaining is fl.7,806,052.60 of which fl.3.7 million is to be paid in taxes, leaving a net profit of fl.4,106,052.60.

* *Ketjen and K.N.Z. have established a holding company—Koninklijke Zout-Ketjen N.V.† Both companies have developed from widely different starting points—Ketjen producing sulphuric acid since 1835 and K.N.Z. extracting salt at Boekelo from 1918 onwards. Since 1947 K.N.Z. and Ketjen have been selling their chemical products through Nederlandsch Verkoopkantoor voor Chemische Producten N.V., in which both companies have a share. Ketjen was also one of the founders in 1954 of N.V. Koninklijke Nederlandse Soda-Industrie, now a wholly-owned subsidiary of K.N.Z. With Cabot Corporation, U.S.A., Ketjen set up Ketjen Carbon N.V.*

† Shareholders in K.N.Z. and Ketjen are to be limited to exchange their shares as follows:—
Fl.1,000 nominal K.N.Z. against fl.1,000 nominal holding company.
Fl.750 nominal Ketjen against fl.375 nominal holding company.

in the "Botlek" area. In this same area K.N.Z. has under construction a salt-electrolysis plant and through Albatros, participates with N.V. Billiton Maatschappij in a company which will produce titanium dioxide.

In 1959 Ketjen participated 63% with American Cyanamid, U.S.A., in Cyanamid-Ketjen N.V., which produces platinum catalysts at Amsterdam. Other subsidiaries are Industriele Maatschappij Activit N.V., which manufactures ion exchange resins.

K.N.Z. acquired Chemische Fabriek Gembo N.V. which at Winschoten and Amsterdam produces waterglass catalysts, detergents, soda and borax, the latter now being among Ketjen's leading products.

The merger of K.N.Z. and Albatros Superfosfaatfabrieken N.V., Utrecht, the latter an important producer of sulphuric acid in the Netherlands, was effected in 1959. K.N.Z. also has a shareholding in Stader Saline G.m.b.H. of Stade, a salt producer.

Reference is made in the K.N.Z.-Ketjen merger announcement to negotiations which are being carried on between K.N.Z. as a shareholder in Albatros, and Bataafse Petroleum Maatschappij N.V. and Koninklije Nederlandsche Hoogovens en Staalfabrieken N.V. as shareholders in Mekog, with a view to arriving at a combination of interests, through a holding company producing synthetic fertilizers. Agreement already reached in principle will take place after the completion of the merger of K.N.Z. and Ketjen.

Courtaulds Group Profit Affected by Increased Competition and Slackening Demand

"Our ability to compete in world markets depends increasingly in efficient and low cost production, and we are doing all we can to maintain our competitive position despite the rising cost of salaries, wages and services."

Sir John Hanbury-Williams
Chairman
Courtaulds Limited

ALTHOUGH captive consumption still largely determines the quantities of sulphuric acid and carbon disulphide produced, Courtaulds Limited are attempting to increase sales of these products to customers outside the group in order to make the maximum use of capacity. According to the annual report 1960-61 these external sales are doing well.

A new plant has been set up at Trafford Park, Manchester, to produce from carbon disulphide carbon tetrachloride for use in the manufacture of fluorocarbons, for which there is a growing market in refrigeration and as propellants in aerosol containers.

The sulphuric acid plant at Glanzstoff-Courtaulds G.m.b.H. has now been in operation for a year and is reported to be operating satisfactorily.

Synthetic Fibres

Higher expenses, greater competition and a slackening of demand have contributed to the decreased group trading profit compared with the previous year. Except for Tricel and Courtelle, fibre demand levelled off during the year as the "near-boom" conditions of 1959 and early 1960 returned to normal. Although retail sales of apparel were maintained, there was no restocking of the production pipeline from fibre to finished goods. Later in the year, demand was also affected by rising imports of fabric.

Although the fall in exports of certain types of fabrics from the United Kingdom has been checked and exports in general of synthetic fibres and yarns continues at a high level, competition is increasing.

Home sales of viscose textile yarn were slightly lower than the previous year. Export markets are so competitive that in some cases the yarn prices obtainable were unprofitable. Recent increases in wages and salaries and in the cost of coal have also affected profit margins adversely.

Trading conditions were particularly difficult for subsidiaries and associates in Canada. Associates in Germany and Italy were less severely affected. Profits of Courtaulds (Australia) were disappointing, being affected by low prices of competing imports of viscose rayon and nylon. Attention is drawn to the inadequacy of the tariff on viscose type yarn and fabric granted in 1954. An application for an effective tariff has again been made.

In the United Kingdom, demand for industrial rayon remained strong, and as a result the Harbens Works at Golborne, scheduled to close last year, continued until March 1961.

The recession in motor car manufacture reduced the sale of tyres as original equipment but the demand for replacements was maintained. The market for commercial vehicles increased after the removal of purchase tax. A yarn with higher strength—Tyrex—is being introduced and further advances are forecast.

Home sales of viscose rayon staple also declined after the record figure of the previous year. Temporary short-time working was introduced at the Greenfield, North Wales, staple factory. In the long term Courtaulds believes that demand for rayon staple will continue to rise.

In the packaging field, the company's subsidiary, British Cellophane Limited, increased its profits and brought additional capacity into production at Barrow-in-Furness where a further expansion is in progress. Exports of Cellophane rose again. An increasing amount of work is being devoted to the technical development of fibres other than cellulose and their uses.

Finance

Group profit from trading was £15,003,262 (£18,025,355 in 1959/60). Group profit from all sources before tax at £18,096,544 compares with the previous year's total of £21,044,043. Some 44% of this came from Courtaulds fabrics and garments and 35% from non-textile activities in packaging, paint, plastics and engineering. The remaining 21% came from raw materials, i.e., chemicals and wood pulp which are produced chiefly for internal use in making fibres, packaging fibres, plastics and paints.

Courtaulds interest in group profit was £9,822,430 as against £11,217,534 for 1959-60 and the parent company's profit was £7,499,279 compared with £9,833,904.

CRUDE SULPHUR IMPORTS INTO WESTERN EUROPE (Average price per metric ton)

SOURCE United States	Finland Jan.-Mar.	Belgium/ Luxembourg Jan.-Mar.	United* Kingdom Jan.-June	Netherlands Jan.-May	Sweden Jan.-Mar.	West Germany† Jan.-Mar.	Norway Jan.-Feb.	Denmark Jan.-May	France Jan.-Mar.
1961	1,524 £11.14	13,495 £9.30	139,478 £9.85	19,924 £8.98		12,716 DM 1128			21,764 £10.24
1960	1,602 £10.86	16,215 £10.61	170,786 £10.35	20,838 £8.97		21,737			n.a.
Mexico									
1961	1,009 £10.82	8,832 £9.05	49,591 £9.84			6,811 DM 1066			11,905 £9.35
1960		26,756 £9.05	42,459 £9.86			21,701			n.a.
France									
1961	8,823 £9.91	12,970 £9.10	80,894 £10.1	15,793 £9.62		12,945 DM 1149			
1960	7,902 £10.91	8,754 £9.51	49,175 £10.45	12,475 £8.96		10,270			
Netherlands									
1961		1,000 £8.88							
1960		1,005 £8.91							
U.S.S.R.									
1961	2,688 £9.44	2,096 £8.77		5,120 £9.36		200 DM 1350			
1960	2,484 £10.86								
TOTAL									
1961	**15,024‡‡ £10.00**	**38,403 £9.12**	**269,973 £9.87**	**40,847‡‡ £9.28**	**20,230 £11.00**	**32,702 DM**	**764 £11.10**	**1,902 £13.96****	**39,908 £10.04**
1960	**15,045‡‡ £11.07**	**53,772 £9.61**	**262,450 £10.12**	**33,368‡‡ £8.98**	**15.645 £11.00**	**53,759**		**1,282 £13.09****	**57,389 £10.08**

‡‡ Excludes small amounts of specialised types of sulphur. ** Includes specialised sulphur.
*Values calculated from customs returns. † Values quoted in DM owing to revaluation in 1961.

PYRITES IMPORTS INTO WESTERN EUROPE

SOURCE	Belgium/ Luxembourg Jan.-March	Denmark Jan.-May	France Jan.-March	Italy Jan.-April	Netherlands Jan.-May	Sweden Jan.-March	West Germany Jan.-March	United Kingdom Jan.-June
Eire								
1961	5,197						4,345	1,845
1960	614							
Italy								
1961					65,140			
1960					76,147		863	
Yugoslavia								
1961								
1960				21,550			2,418	
Norway								
1961					12,417		67,677	
1960					8,856		97,569	
Portugal								
1961	33,029		6,025		10,132		14,187	
1960	52,130		n.a.		41,434		31,316	
Sweden								
1961								14,037
1960								11,462
Finland								
1961							32,369	
1960							8,648	
Spain								
1961	37,940		76,363		6,375		143,615	11,164
1960	63,539		n.a.		19,249		104,665	5,514
Turkey								
1961							16,900	
1960							11,528	
Cyprus								
1961	8,700		47,023		21,092		59,822	107,664
1960	22,336		n.a.	45,549	28,221		100,135	98,336
Greece								
1961								
1960					10,930			
Algeria								
1961			4,283					
1960			n.a.					
Total								
1961	**85,610**	**37,547**	**133,694**		**115,172**	**10,608**	**338,975**	**132,865**
1960	**138,619**	**56,206**	**127,250**	**71,428**	**184,836**	**8,237**	**357,141**	**117,249**

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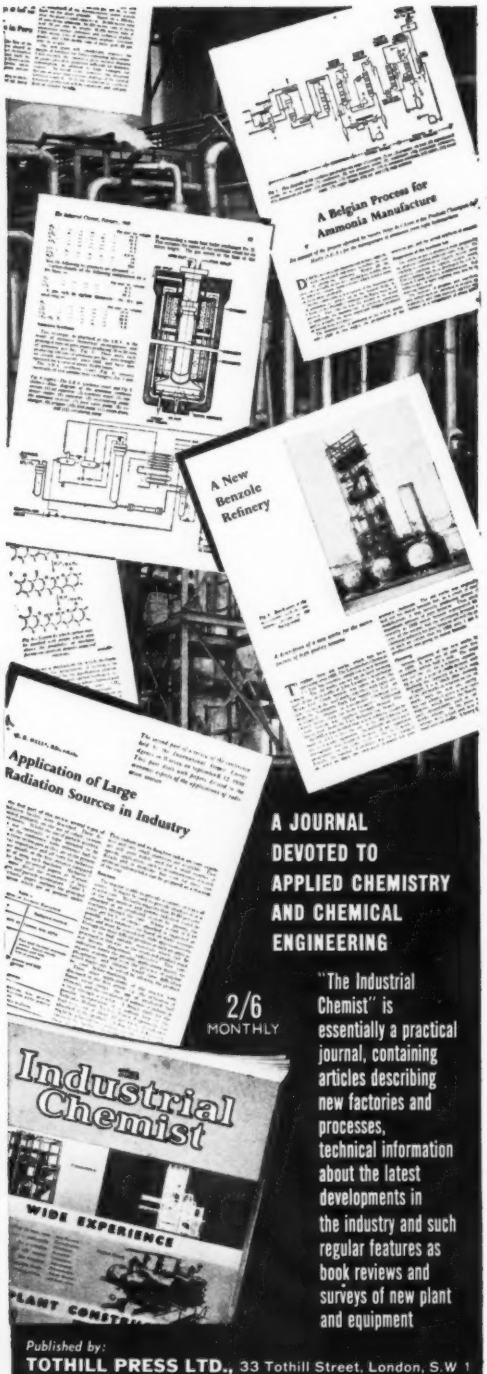
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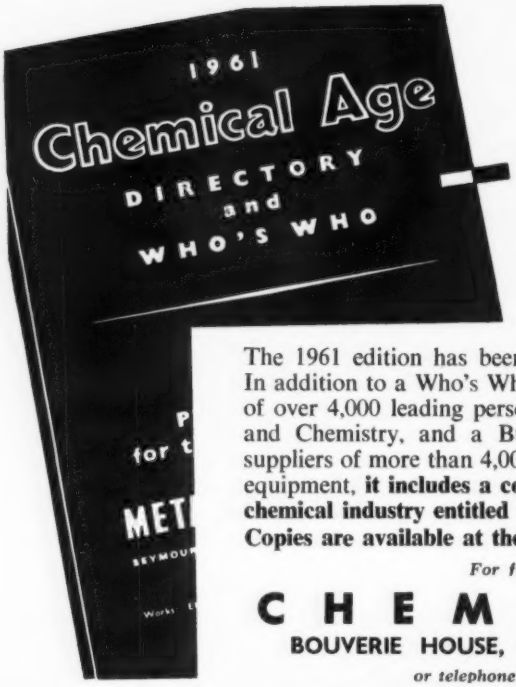

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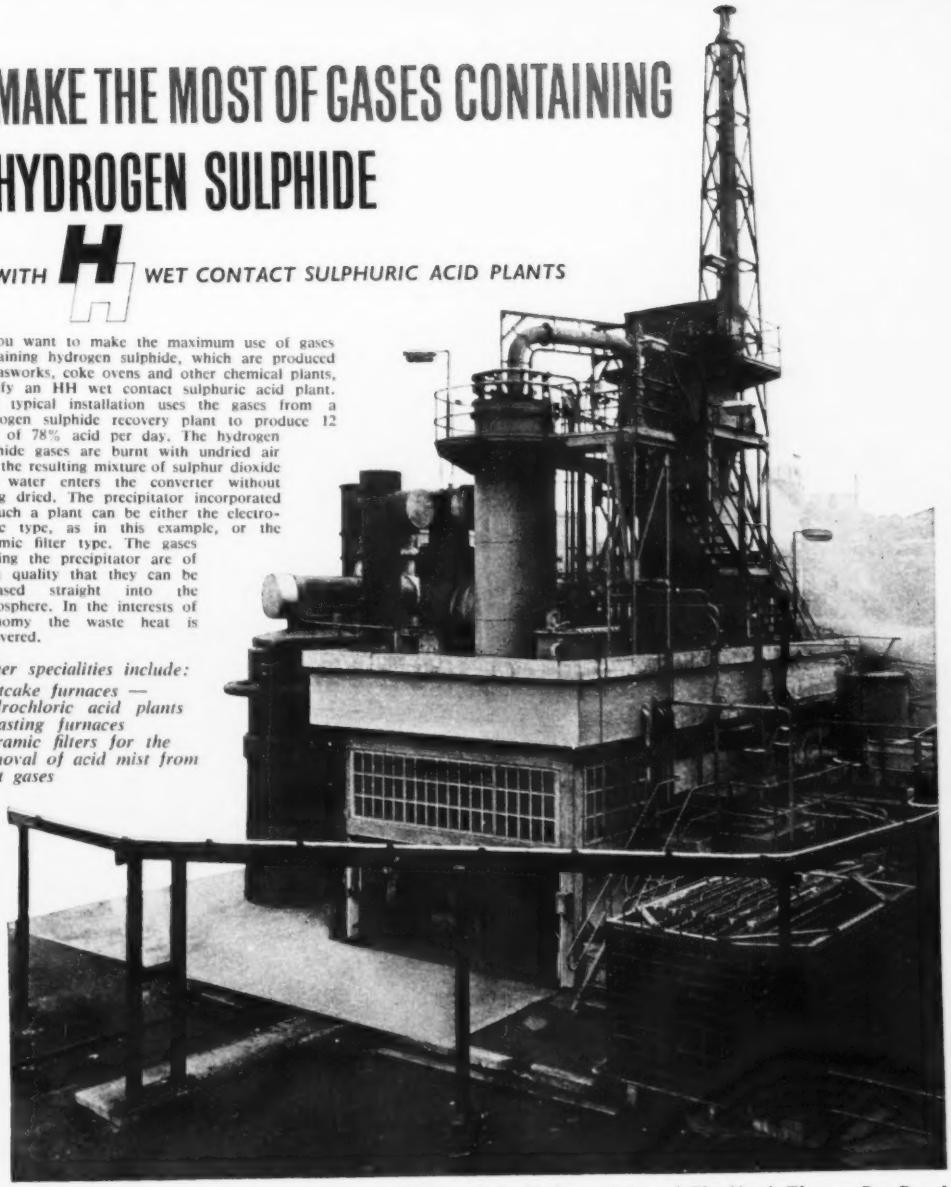

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